ENVIRONMENTAL ASSESSMENT AND BIOMONITORING OF THE TWELVE MILE CREEK WATERSHED, NIAGARA PENINSULA, ONTARIO

by

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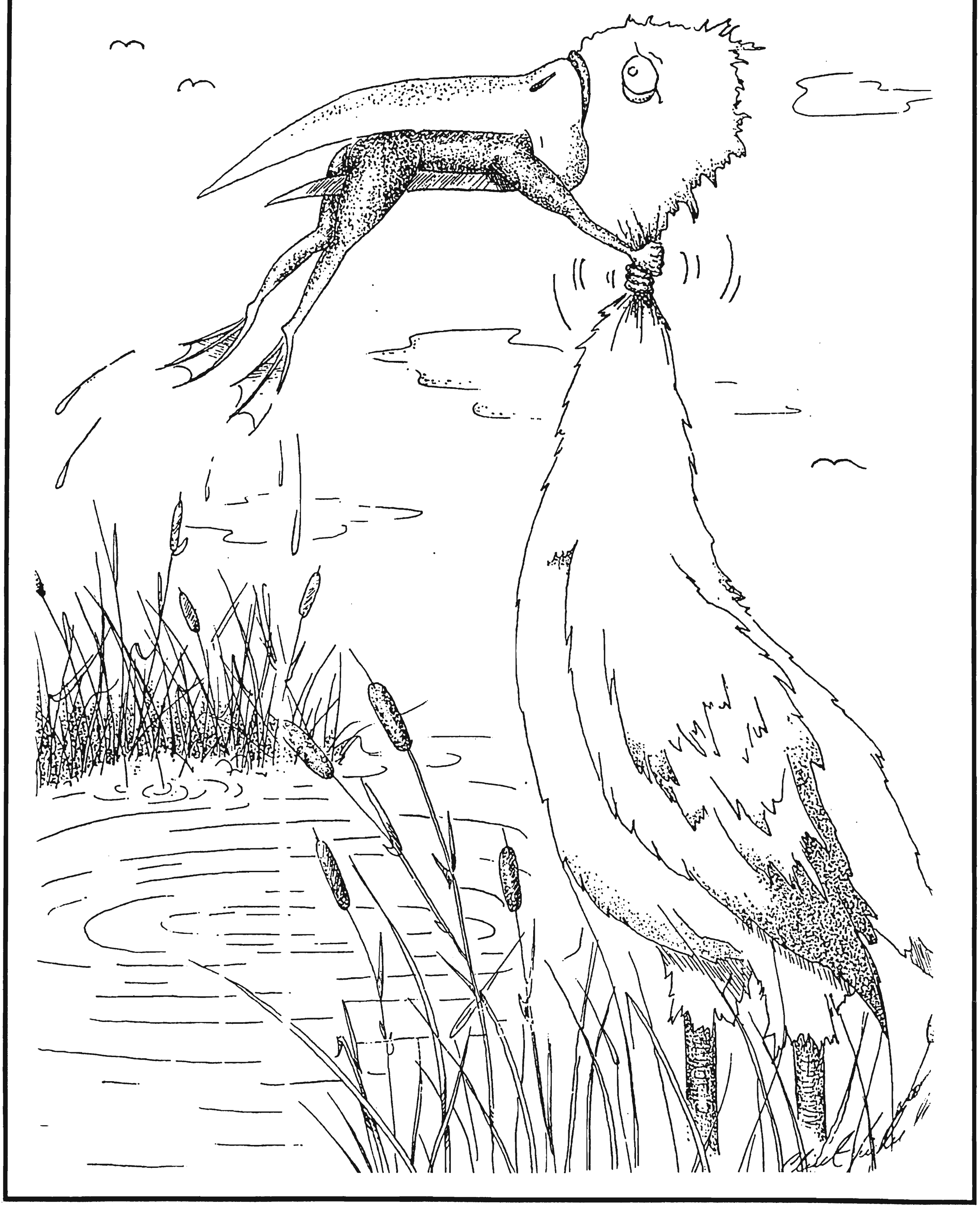

ABSTRACT

In light of the heavy reliance of the people of the Niagara Peninsula on the Twelve Mile Creek (TMC) watershed for recreational activities and for municipal and industrial uses (e.g., drinking water, shipping and discharge of effluents), it was deemed prudent to assess the environmental health of the system by analysing the sediments total and exchangeable metal, and TPH contents. The MOEE has set guidelines with limits for the protection and management of aquatic sediments, and the sediments from the headwaters of the TMC have total metal and TPH (subset of O&G) contents well below the lower provincial limits. Areas of environmental concern where total metal contents in sediments, either individually or collectively, exceed the guideline, are the south side of Lake Gibson, the Old Welland Canal, a segment of TMC just south of the QEW and Martindale Pond. The total metal content of sediments does not in all instances identify areas of biological concern. Instead, it has been found that the exchangeable metal fraction of sediments is a better indicator of metal availability and thus potential accumulation in organisms. In some instances, the exchangeable metal fraction agrees with the total metal fraction defining areas of environmental concern, but it does vary from site to site reflecting the natural variability of the ambient environment. Overall, the exchangeable metal fraction of sediments appears to be a better indicator of anthropogenic pollution and ecosystem impact.

A histochemical study of *Anodonta* sp., *Elliptio* sp. and zebra mussels (*Dreissena polymorpha)* was done in conjunction with passive biomonitoring of zebra and quagga mussels (*Dreissena bugensis*) from the Twelve Mile Creek watershed and Lake St. Clair (Jeanette's Creek, Chatham, Ontario). The highest concentrations of divalent metals such as Cu, Ni, Cd, and Zn, and trivalent Al appear to accumulate in gill and kidney tissues. Metal contents of organ tissues in *Anodonta* sp. vary with size class. Organ metal content varies

among size classes, thus requiring consideration of size in biomonitoring studies. Shucked zebra and quagga mussel tissues, exhibited similar size class to Al content trends. In addition they reflected the Al content trends of top (approximately 10 cm) most sediments in the Twelve Mile Creek watershed. Quagga mussels appear to have higher Al concentrations than zebra mussels, thus suggesting that quagga mussels may be better passive biomonitors of Al. Cd content in zebra mussel tissues, seemed to increase with size class trends. This was not demonstrated in the quagga mussel tissues. This suggests that Cd may be regulated by quagga mussels and not by zebra mussels, and that zebra mussels may be better passive biomonitors of Cd than are quagga mussels.

Zebra mussel, quagga mussel, *Anodonta* sp., and *Elliptio* sp. were used in a two part, active (translocated) biomonitoring study of the Twelve Mile Creek watershed. There was no statistical difference in death rates between zebra and quagga mussels after 65 days of biomonitoring. However there does appear to be a difference of death rates between sites. Unfortunately the data base did not permit us to differentiate between sites. Relative to Port Colborne Harbour (Port Colborne, Ontario), the Twelve Mile Creek watershed appears to be elevated in bioavailable Al. An area near the terminus of the Twelve Mile Creek appears to be an area of environmental concern since mussels seemed to have accumulated relatively large concentrations of Cd, Zn, and Pb. In addition to possible metal loading from a nearby outfalls, or possible upstream outfalls, road salt runoff from storm sewers may have contributed to metal accumulation through cation exchanges processes. Similar trends in cumulative quagga mussel metal concentrations during the two time periods (65 and 159 days), suggest that quagga mussels may reach equilibrium within 65 days of translocation. Differences in bioaccumulated metal concentrations of the two dreissenid species demonstrate that active biomonitoring studies must use a variety of organisms to adequately assess the environmental situation of specific waterways and/or bodies.

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ABSTRACT

In light of the heavy reliance of the people of the Niagara Peninsula on the Twelve Mile Creek (TMC) watershed for recreational activities and for municipal and industrial uses (e.g., drinking water, shipping, and discharge of effluents), it was deemed prudent to assess the environmental health of the system by analysing the sediments total and exchangeable metal, and TPH contents. The MOEE has set guidelines with limits for the protection and management of aquatic sediments. The sediments from the headwaters of the TMC have total metal and TPH (subset of O&G) contents well below the lower provincial limits. Areas of environmental concern where total metal contents in sediments, either individually or collectively, exceed the guideline, are the south side of Lake Gibson, the Old Welland Canal, a segment of TMC just south of the QEW and Martindale Pond. The total metal content of sediments does not in all instances identify areas of biological concern. Instead, it has been found that exchangeable metal fraction of sediments is a better indicator of metal availability and thus potential accumulation in organisms. In some instances, the exchangeable metal fraction agrees with the total metal fraction defining areas of environmental concern, but it does vary from site to site reflecting the natural variability of the ambient environment. Overall, the exchangeable metal fraction of sediments appears to be a better indicator of anthropogenic pollution and ecosystem impact.

INTRODUCTION

Before anthropogenic intervention and modification, Twelve Mile Creek (TMC) was a cold water creek with its headwaters in Short Hills Provincial Park (SHPP). The creek meandered naturally downstream to a flood plain (the north end of what is now known as Martindale Pond) and emptied into Lake Ontario. In the early 1800's, shipping activity and industrialization followed the growth of Port Dalhousie. In 1829, the first Welland canal opened and was operated using the natural TMC banks as a tow path. The second canal opened in 1845 and replaced the original one. A dam was built at the north end of the canal (near Lake Ontario) promoting the flooding of the lands to create what is now known as Martindale Pond. Shipping in canals 1 and 2 passed through locks of the Old Welland Canal (OWC; Figure 1), which prior to the construction of the Highway 406 flowed openly into TMC. In the mid 1870's a third canal was built, which unlike the second, did not use the OWC locks and only passed through the north east corner of Martindale Pond. Remnants of the opening of the third canal into Martindale Pond can still be seen near combined sewer overflow outfalls 1606/1622/1624 (Figure 1). In 1913, a fourth canal (the modern Welland Canal) was opened to replace canals 2 and 3, thus ending the historical importance of the shipping industry in TMC and Martindale Pond.

In 1896, the construction of the Decew Falls power generating station was completed. This station is still in operation. Diverted waters from the Welland Canal form Lake Gibson and Lake Moodie and eventually descend over the falls at Decew. TMC was straightened to accommodate the increased water volume and to minimize flooding.

During the early 1900's, due to the limited use by the shipping industry, a rowing course was built in Martindale Pond. High rates of sedimentation threatened the use of the course. In 1930, the rowing course was dredged and the material spread within a 900 m radius of the point of collection. Thirty four years later (1964) the course was dredged again and the material was used to create Henley Island and Michael Rennie Park.

The TMC watershed serves as a "sink" for discharges from storm sewers, combined sewers, combined sewer overflows, and industrial sewer, (Figures 1 and 2). Of particular interest are the industrial discharge sites. There are three known areas of industrial discharge along the OWC, two of which originate from paper plants (Ontario Paper Co. Ltd, Fraser Paper Inc., and Kimberly-Clark of Canada Ltd), and one is near the terminus of TMC, where General Motors Plant 4 has an outfall.

Numerous other potential non point-sources of contamination are found within the watershed. Eleven landfills exist within the St. Catharines-Thorold area of the watershed. Of these, a closed Thorold landfill is located in the headwater area of TMC at the base of Rice Road. Another large former municipal landfill exists just below Decew Falls (Rotary Park) adjacent to TMC. A former industrial landfill site used by General Motors of Canada is located adjacent to the eastern bank of TMC, downstream of Highway 406 and upstream of the QEW. As mentioned above, Henley Island in Martindale Pond and Michael Rennie Park at the north end of the Pond, are also former landfill, filled mostly with dredged material from Martindale Pond. A non-industrial former landfill site (Ontario Street) exists between the entrance of the third canal into Martindale Pond and Ontario Street. The former Grantham Township landfill (non-industrial) is in line with the Ontario Street site and the third canal

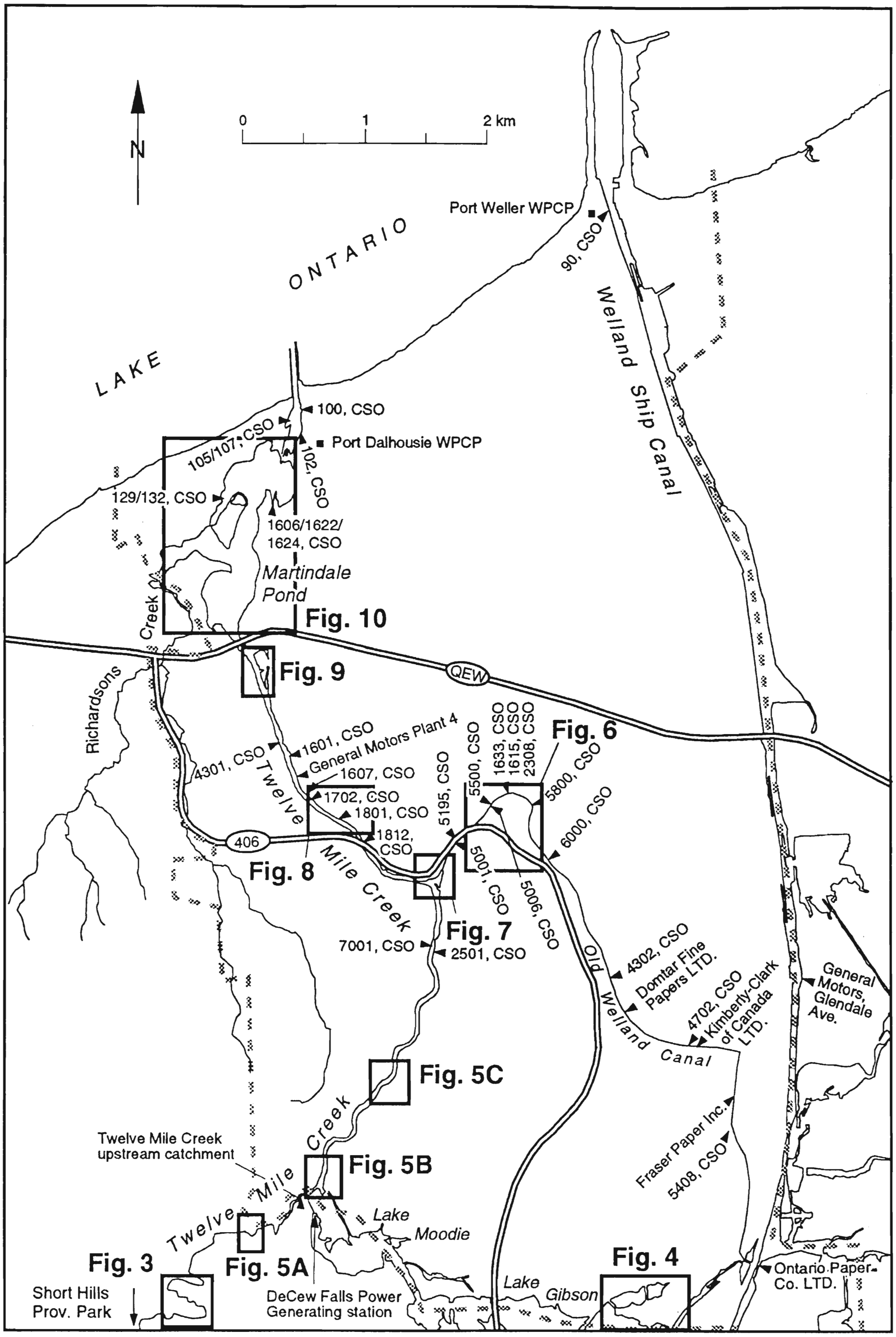


Figure 1. Locality map of Twelve Mile Creek watershed in vicinity of St. Catharines, Ontario. Arrows with numbers represent combined sewer overflow (CSO) outfalls and industrial outfalls emptying into local water bodies.

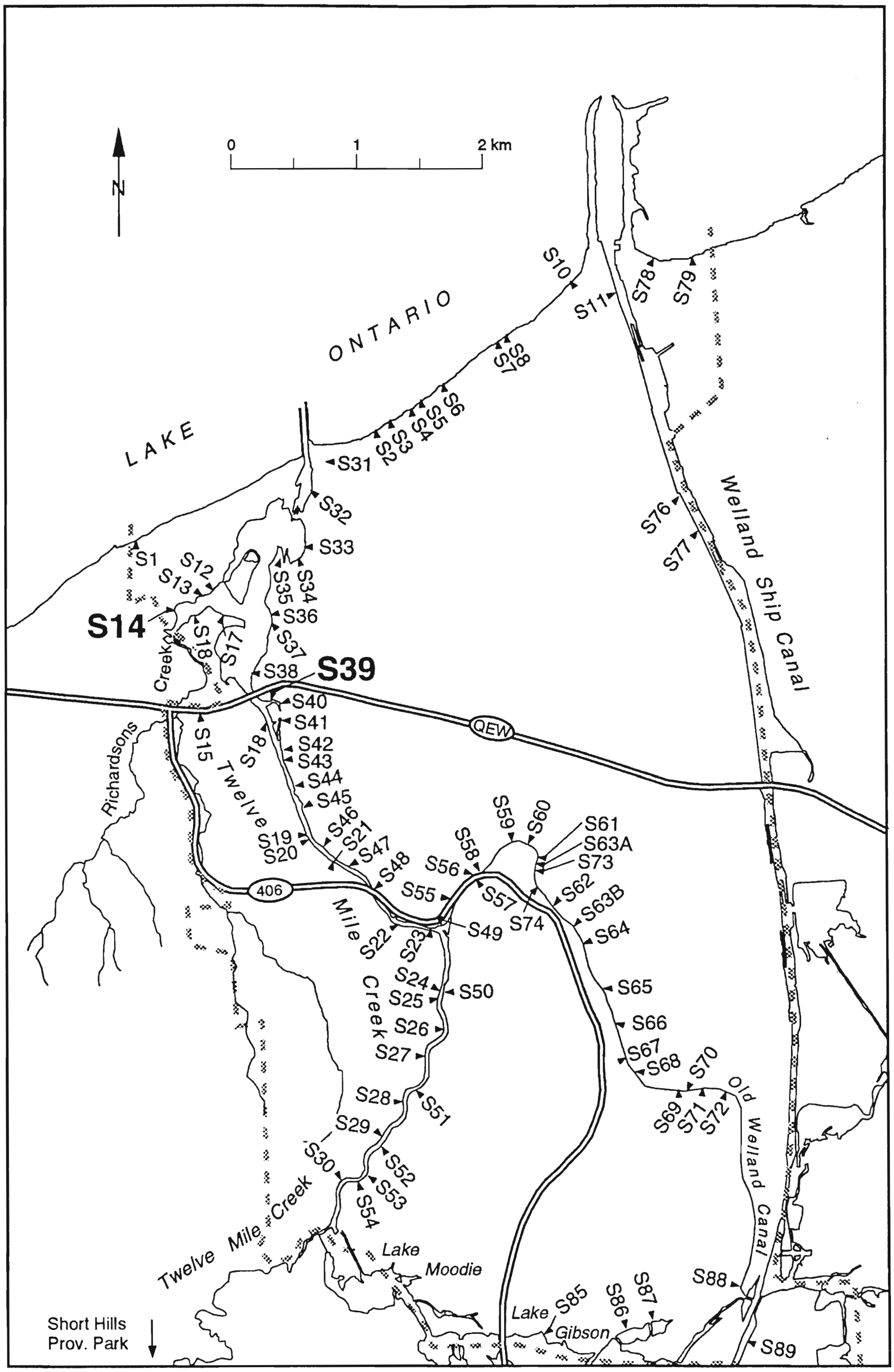


Figure 2. Locality map of Twelve Mile Creek watershed in vicinity of St. Catharines, Ontario. Arrows with numbers represent municipal storm sewer outfalls.

route. Along the eastern banks of the Old Welland Canal, there are four former landfills within 2 km of each other. Two of these former landfills served industry (Shawinigan Chemical Company and Domtar Fine Papers Ltd). The other two were non-industrial and are located in Clifford's Creek Park and in a Municipal Golf Course.

Industry has played a major role in the economic development and prosperity of the Niagara Region. However, this development comes with a price where these industries may impact on the environment and thus the quality of life of its inhabitants. Our increasing awareness of environmental concerns calls for industrial development and sustainability within a sound ecological and environmental strategy. To fulfill this mandate of a sound and sustainable strategy, a data must be established that identifies areas of environmental concern. These concerns may specifically address present-day events or events that have a longer temporal aspect. The identification of contaminants in the fluvial environment may be one area that deserves study, because rivers traditionally serve as avenues of industrial discharge while supplying drinking waters to urban centers. This dichotomy of use demands a strict supervision on the discharges as these indirectly or directly may have an impact on human health, but most certainly on that of the aquatic fauna and flora. Over the past few decades the provincial and federal governments have passed, revised and updated rules, regulations, and guidelines to protect the various ecosystems and ultimately our well-being. These guidelines are constantly revised as our understanding of sub-lethal and lethal effects of the various contaminants increases. A downfall of the Canadian Environmental Guidelines, with the exception of the CCME water guidelines, is that they do not distinguish between species of heavy metals, and only a few heavy metals such as Al, Cd, Cr, Cu, Ni, and Pb actually have specific guidelines. The CCME (1991) guidelines regulate Al concentrations for aquatic life, while the Guidelines for the Protection of Aquatic Sediment Quality in Ontario (Persaud *et al.*, 1992) does not. Since half of this thesis deals with aquatic invertebrates, an arbitrary value was set for total Al concentration. The lowest Al concentrations were found in Johnston Harbour sediments near Tobermory (Lake Huron) which is a cottage area free of industrial discharge. The bedrock in this area is a limestone which has very little aluminum in comparison to clay forming minerals, such as K-Feldspar. The bedrock is covered by a very thin layer of soil, which upon visual inspection has a low clay component. Thus, this material seemed a most likely candidate for setting an Al guideline since the Niagara Escarpment consist, mainly of dolomite and sandstone, with relatively few minerals which may contribute some Al. Therefore, a lowest effect level (LEL) for Al was set at approximately 150% (46,000 ppm) of the Johnston Harbour grab sample value, and the severe effect level (SEL) was set at twice this amount with 92,000 ppm.

The TMC watershed is of major importance to the well-being of the Niagara Region. It serves as a source of drinking water, is an area of recreation, and it generates hydro-electric power, but also is used for various activities such as shipping and effluent discharges.

This interdependence on the watershed for sustainable industrial and recreational developments, demands that an assessment be carried out to determine the overall environmental health of the system. To this end, the study will be a first attempt to establish an environmental database of both present and past human activity in the region, specifically the TMC watershed. This study will test for the following environmental parameters: Water quality (pH, conductivity, turbidity, dissolved oxygen, temperature, salinity, nitrogen-ammonia), TPH (total petroleum hydrocarbons), and total and exchangeable metal content in sediments from cores obtained throughout the watershed. These data will be evaluated with respect to the appropriate provincial or federal guidelines to assess the environmental health of the sediments. Furthermore, it is hoped that this database will serve as a building block in establishing firm and comprehensive guidelines in the future in dealing with all aspects of the development of the region.

METHODS

Quality Assurance and Control

All glassware, bottles, and teflon beakers were cleaned using aqua regia, and rinsed in distilled and quadruply-deionized water after each use. All sampling instruments were cleaned using distilled and quadruply-deionized water. Laboratory handling equipment, such as knives and spatulas, were rinsed in quadruply-deionized water before use. Analytical grade (AnalR) $HClO_4$ and HF were used. Analytical grade HNO_3 was distilled in a quartz still to remove more impurities. Good standard laboratory techniques were practised and every attempt was made to ensure methodologies followed E.P.A. or MOEE protocol.

Quality control was accomplished using blank and duplicate samples. Percent accuracy for total metal content in sediments was determined using NBS SRM 2704 (Buffalo River Sediment; Keith *et al*, 1983). Total petroleum hydrocarbon spike recovery was calculated from the addition of pure motor oil. Precision for biological samples (discussed in Chapters 2 and 3) was calculated by using duplicate samples (Table 1).

Table 1. Accuracy, recovery and precision are in %, for sediment, NBS 2704, motor oil and biological tissue samples.

Material	Ni	Cu	Al	Cr	Cd	Pb	Zn	As	Se	Co	Be	Mo	TPH
Sediment (Total)	4.14	1.57	2.46	1.85	10.46	3.47	5.58	12.73	25.3				
Sediment (Exchangeable)	29.15	8.15	21.23		14.61	12.89							
NBS 2704	104.13	80.15	82.11	95.09	78.03	92.43	97.44	95.29	103.27				
Sediment (TPH)													14.55
Motor Oil													95.00
QM Tissue[a]	4.58	4.14	10.45	11.39	8.92	20.25	7.03						
ZM Tissue[a]	4.55	3.24	13.27	8.39	11.55	19.86	2.85						
ZM Tissue[b]	7.66	8.31	19.86	22.47	16.64	28.48	5.69			20.04	25.28	26.22	
ZM Tissue[c]	9.27	7.49	11.15	31.43	3.06	26.18	3.97						
QM Tissue[c]	10.58	2.28	8.56	32.57	4.44	22.24	4.01						
QM Tissue[d]	3.84	5.13	6.57	10.27	4.61	9.14	2.69						
Anodonta and *Elliptio*													
Muscle		15.30	16.42		18.33	47.18	5.97						
Mantle	24.80	2.46	24.18	8.81	0.37	7.18	17.01						
Kidney	49.82	16.59	48.68	10.04	1.11	33.09	3.24						
Gut	39.51	6.29	31.08	23.23	2.34	33.10	2.97						
Gill	7.61	19.36	9.01	9.46	2.54	24.11	2.65						
Foot		12.47			26.55	17.73	4.72						

Note: QM and ZM represent quagga and zebra mussels, respectively. [a] Passive biomonitoring in the Twelve Mile Creek Watershed. [b] Passive biomonitoring in Jeanette's Creek. [c] Active biomonitoring (65 days). [d] Active biomonitoring (159 days).

Sample Areas

Areas sampled were chosen for their geographic distribution, ease of access, and their hydrologic conditions. The main focus of the sampling strategy was to obtain samples representative of the Twelve Mile Creek watershed extending from Lake Gibson (a waterway associated with the Welland Canal system), Short Hills Provincial Park (SHPP), the natural headwater area of the creek, to Martindale Pond (Figure 1). Sediment sampling was done using two different coring samplers. A stainless steel 1.8 m Livingston corer, fitted with a plastic sleeve, was used for deep coring. A small 30 cm hand held corer fitted with plastic sleeves was used for shallow coring. In addition, 35 cores and 2 grab samples were collected from Port Colborne Harbour (Lake Erie sampled Oct. 25/94) and Johnston Harbour (Lake Huron sampled Oct. 26/94) for reference and background parameters. In addition, one small core (30 cm) was taken at the mouth of Jeanette's Creek (Lake St. Clair, sampled Oct. 15/94). The majority of the smaller cores (< 30 cm) were sampled on September 24/94 by shore access. The seven larger cores, ranging from 34 to 110 cm, were sampled by boat on Martindale Pond. In addition, cores A, B, and C were sampled by boat. Cores obtained from Martindale Pond were sampled on December 13, 1994. Immediately upon removal of the corer from the water, the sleeve with the sediment was removed, capped, labelled, and transported to the lab.

Engineered streams, which are relatively straight, instead of curving (in a loose sense 'meandering'), flow at an accelerated rate thus minimizing sedimentation and maximizing transport of material. Consequently, due to the engineered nature of the river and creek beds in this study, it was often difficult to obtain full core samples. In addition, the unsafe and inaccessible shore at some localities hampered sampling of Twelve Mile Creek.

In addition to sediment samples, water quality readings, pH, conductivity (mS), turbidity (NTU), dissolved oxygen (mg/kg), temperature (°C), salinity (%), were obtained using a Horiba "Water Checker" (model U-10) and Hach Kit spectrophotometer (model 3200) for Nessler nitrogen-ammonia (mg/kg) measurements. This aids in identifying changes in water quality.

Core Sediment Preparation

Frozen sediment cores were extruded from the core sleeve using a stainless steel rod. Samples were taken from the center of the core to minimize smudging and cross sample contamination. Top and bottom portions of each core were sampled, and additional samples were taken from distinct lithological intervals. Each lithological interval was measured and described (Appendix 1). Samples were placed into glass beakers and freeze dried. The freeze-drying process lasted 2 days. Sediments were then disaggregated using a clean test tube as a pestle. The separation was performed carefully to avoid crushing the sediment particles. Sediments were then sieved into three size fractions (> 150 μm, < 150 μm and < 62.5 μm). Only the fine sediment fraction (< 150 μm) was used for chemical analysis. A total of 163 samples were prepared for environmental testing.

Total Petroleum Hydrocarbons (TPH)

An environmental assessment of sediments would not be complete without an organic compound evaluation. Although significant or measurable organic contaminants may not be detected in a water sample, it can not be used to represent the sediment conditions. Most organic compounds will either become part of the biotic system or the sediment column. Fatty acids in organism tissues act as reservoirs for organic contaminants; however, a large percentage can adhere to sediment surfaces. This is a very important consideration when dealing with particulate matter in turbulent creeks, such as TMC. The greater the residence time and available surface area, the greater the probability of grain coating. Once a particle is coated, it may fall out of suspension and become buried, which is true of both organic (i.e., phytoplankton) and inorganic (e.g., clays such as kaolinite) particulates.

Core samples were randomly chosen for TPH, in an attempt to cover as much of the watershed as possible. A modified TPH test (APHA, WWA and WEF, 1992) was used to analyse samples. Sediment (< 150 μm) samples ranging from 180 mg to 5.5 g were placed into clean bottles into which 20 mL of hexane was added. The bottles were then capped and securely tightened to prevent evaporation. The extraction was accelerated by shaking for 15 minutes and by placing the bottles into a sonic bath for 5 minutes. The samples were then poured into a filter containing glass wool (used as a plug), 1 g of silica gel (mesh 100 - 200) for passing only the non-polar hydrocarbons, and 1 g Na_2SO_3 for removing any water. Separated fractions were collected in preweighed weighing pans. This process was repeated 3 times. The TPH concentrations were determined gravimetrically. Percent recovery was determined by using a spiked sample of 0.10 g pure motor oil and blank samples. Duplicate samples were used to calculate percent error (Table 1).

Total Metal Analysis

The entire set of sediments (163) collected in the study, with the exception of those from Centennial Creek and Old Welland Canal, were analyzed for nine elements. Only the less than 62.5 μm sediment fraction was tested. A 0.25 g subsample was weighed to four decimal places into teflon beakers. The samples were digested, following U.S. EPA method

3050, in a 30 mL mixture of $HF:HClO_4:HNO_3$ (8:1:1) and placed on a covered hot plate set at medium for 48 hours. Twenty five mL of 7% HNO_3 was added to the beakers which were then placed on a hot plate for an additional 3 to 5 minutes, until any remaining dark material had gone into solution. Samples were then filtered into 25 mL volumetric flasks using medium porosity ashless filter papers and diluted to mark using quadruply deionized water. Filtrates were poured into clean bottles, tightly capped and stored in the fridge (4 °C) until analysis. A Varian Spectra AA-400P Atomic Absorption Spectrometer (AAS) was used for metal analysis. Air/acetylene flame conditions were used for the analysis of Ni, Cu and Zn, while Cd and Pb were analyzed using an ACT tube placed on top of the burner increasing residence time and thus atomizing conditions. The analysis of Al and Cr required a NO_2/acetylene flame for higher atomizing temperatures. As and Se were analyzed using a graphite furnace attachment.

Accuracy and precision were determined using prescribed parameters through the use of replicates and NBS, SRM (National Bureau of Standards, Standard Reference Material) 2704 analysis (Buffalo River Sediment; Keith *et al.*, 1983; Table 1). The filter papers were ashed at 500 °C for 1 hour and allowed to cool in a desiccator. Remaining ash was then weighed and noted for concentration weight calculations.

Exchangeable Metal Analysis

Exchangeable metal fraction was determined for six elements using a modified first step of Tessier *et al.*'s (1979) selective sequential extraction technique. Analytical grade $MgCl_2 \cdot 6H_2O$ (256 mg) was added to water. The pH of the solution was adjusted to 7 using NaOH resulting in the precipitation of some Pb, Fe, and Al salts and purification of the solution. Approximately 0.25 g of each sample was weighed into polysulfone centrifuge tubes, 10 mL of the salt solution was added and capped. Tubes were placed vertically, to prevent spillage, on a shaker and agitated for 3.5 hours. Periodically (every half hour) individual samples were removed and hand shaken to ensure complete cation exchange.

Samples were then filtered through medium porosity and speed filter paper. The filtrate was collected into Pyrex test tubes, sealed and stored at 4 °C until analysis. Analyses were performed using AAS techniques previously described (see **Total Metal Analysis**).

Concentrations were calculated by adjusting salt solution ratios to 1 M. Percent error (precision) was calculated using duplicate samples (Table 1).

RESULTS

Water Quality

Water quality data were recorded at a number of sites throughout the year (Table 2). Due to the limited sources of input into the TMC within the head water region, it is feasible to compare Short Hills Park water quality data to sites representing other areas of the watershed. Consistently high water temperature, conductivity, salinity and nitrogen-ammonia readings were recorded at site 18; this site is part of the Old Welland Canal system. In addition, water tested at site 18 on January 13, 1995 and February 20, 1995 had low dissolved oxygen contents. Water quality at sites 21 and 22, representing the segment of TMC just upstream of Martindale Pond varied throughout of the year. For example, water turbidity at site 21 was high on September 29, 1994 and dissolved oxygen content was low on December 21, 1994. Water quality at site 22 on January 13, 1995, exhibited high conductivity and salinity. In addition, water at site 22, on April 17, 1995, was relatively low in dissolved oxygen. Water tested at site 16, representing the north west region of Martindale Pond near Michael Rennie Park, had variable turbidity which and ranged from a high 157 (NTU) of to undetectable (NTU) on December 21, 1994 and April 4, 1995, respectively.

Sediments

With the exception of samples tested for Total Petroleum Hydrocarbons, only selected high metal values from each core are presented in relation to the Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario (Persaud *et al.*, 1992). This provides an overall picture of the distribution of contaminants within Twelve Mile Creek watershed sediments (Appendix 1).

Table 2. Water Quality Data at selected TMC watershed sites such as pH, conductivity (Cond.), turbidity (Turb.), dissolved oxygen (DO), Temperature (Temp.), Salinity (Sal.), and Nitrogen Ammonia (NH_3-N).

Site	pH	Cond.	Turb.	DO	Temp.	Sal.	NH_3-N
		(mS)	(NTU)	(mg/L)	(°C)	(%)	(mg/kg)
29/9/94							
SHPP (34A)	7.62	0.46	40	8.7	12.5	0.01	N.D.
Decew	7.87	0.22	18	10.0	16.6	0.00	N.D.
Glendale (30)	7.74	0.29	16	9.8	17.4	0.00	N.D.
Site 18	7.55	0.44	18	8.7	**20.8**	0.01	N.D.
Capri (22)	7.64	0.24	16	10.1	16.6	0.00	N.D.
Site 21	6.94	0.32	**115**	**7.7**	13.2	0.01	N.D.
21/12/94							
SHPP (33)	7.96	0.49	12	13.4	3.9	0.00	N.D.
Decew	7.94	0.22	22	13.4	4.2	0.00	N.D.
Glendale (30)	7.97	0.22	24	13.5	4.2	0.00	N.D.
Niagara	7.97	0.22	19	13.6	4.3	0.00	N.D.
Site 21	7.53	0.31	34	**12.0**	3.4	0.01	N.D.
Site 16	7.79	0.22	**157**	13.2	7.5	0.00	N.D.
13/1/95							
SHPP (33)	7.97	0.37	50	12.6	2.6	0.01	0.05
Decew	7.64	0.24	N.D.	14.2	1.3	0.00	N.D.
Glendale (30)	7.92	0.23	N.D.	14.7	1.3	0.00	N.D.
Site 18	7.67	**1.74**	30	**12.9**	**7.4**	**0.07**	**0.39**
Capri (22)	7.77	**1.8**	N.D.	12.5	3.0	**0.06**	N.D.
Site 10	7.99	0.24	N.D.	14.1	0.8	0.00	N.D.
Site 16	8.00	0.22	N.D.	13.2	0.9	0.00	N.D.
20/02/95							
SHPP (33)	7.78	0.44	71	13.0	0.5	0.01	0.19
Decew	7.68	0.23	2	13.8	0.6	0.00	N.D.
Glendale (30)	7.74	0.23	5	13.5	0.6	0.00	N.D.
Site 18	7.62	**0.42**	15	**11.3**	**8.0**	0.01	**1.51**
Site 21	7.40	0.25	9	12.6	0.6	0.00	N.D.
Site 10	7.63	0.24	19	13.3	0.4	0.00	N.D.
17/04/95							
SHPP (33)	7.99	0.25	5	14.4	6.5	0.00	N.D.
Decew	8.00	0.22	12	15.0	2.1	0.00	N.D.
Glendale (30)	7.96	0.22	10	14.0	2.2	0.00	N.D.
Capri (22)	7.40	0.25	9	**12.6**	0.6	0.00	N.D.
Site 10	7.99	0.24	16	14.5	4.7	0.00	N.D.
Site 16	7.99	0.22	**0**	14.4	4.0	0.00	N.D.

Note: Bold numbers represent high or low water quality site conditions. ND = not determined.

Total Petroleum Hydrocarbons

The Guidelines for the Protection and Management of Aquatic Sediment Quality of Ontario (Persaud *et al.*, 1992) set a guideline for open water disposal of sediments, at an oil & grease (O&G) content of 0.15 %, which includes vegetable, animal and minerals oils. Instead of the O&G test, TPH (Total Petroleum Hydrocarbons) is a more definitive test of organic pollutant loading because it determines only the non-volatile and non-polar hydrocarbon content (mineral oils and greases) of sediments. Since O&G includes TPH and no guidelines have been set for TPH, it is reasonable to assume that applying the 0.15 % O&G limit to TPH determinations would reveal areas of detrimental impact loading and err on the high side.

Short Hills Provincial Park. Two (34B and 34C) of the three sediment cores from the headwaters of Twelve Mile Creek in Short Hills Provincial Park (SHPP) were analyzed for their TPH content (Figure 3). Their contents are less than 14 mg/kg, which is well below the Provincial guideline of 1500 mg/kg.

Lake Gibson. All three cores from Lake Gibson were tested for their TPH content (Figure 4). Sediments in cores 37 and 38 are directly impacted by storm water effluents draining the Confederation Heights subdivision of Thorold, while the sediments of core 39 are impacted by waters diverted from the Welland Canal and Beaverdams Village. TPH values in cores 37 (236 mg/kg) and 38 (252 mg/kg) are well below the Provincial guideline of 1500 mg/kg, whereas those of core 39, which range from 11,256 to 24,834 mg/kg, greatly exceed the guideline.

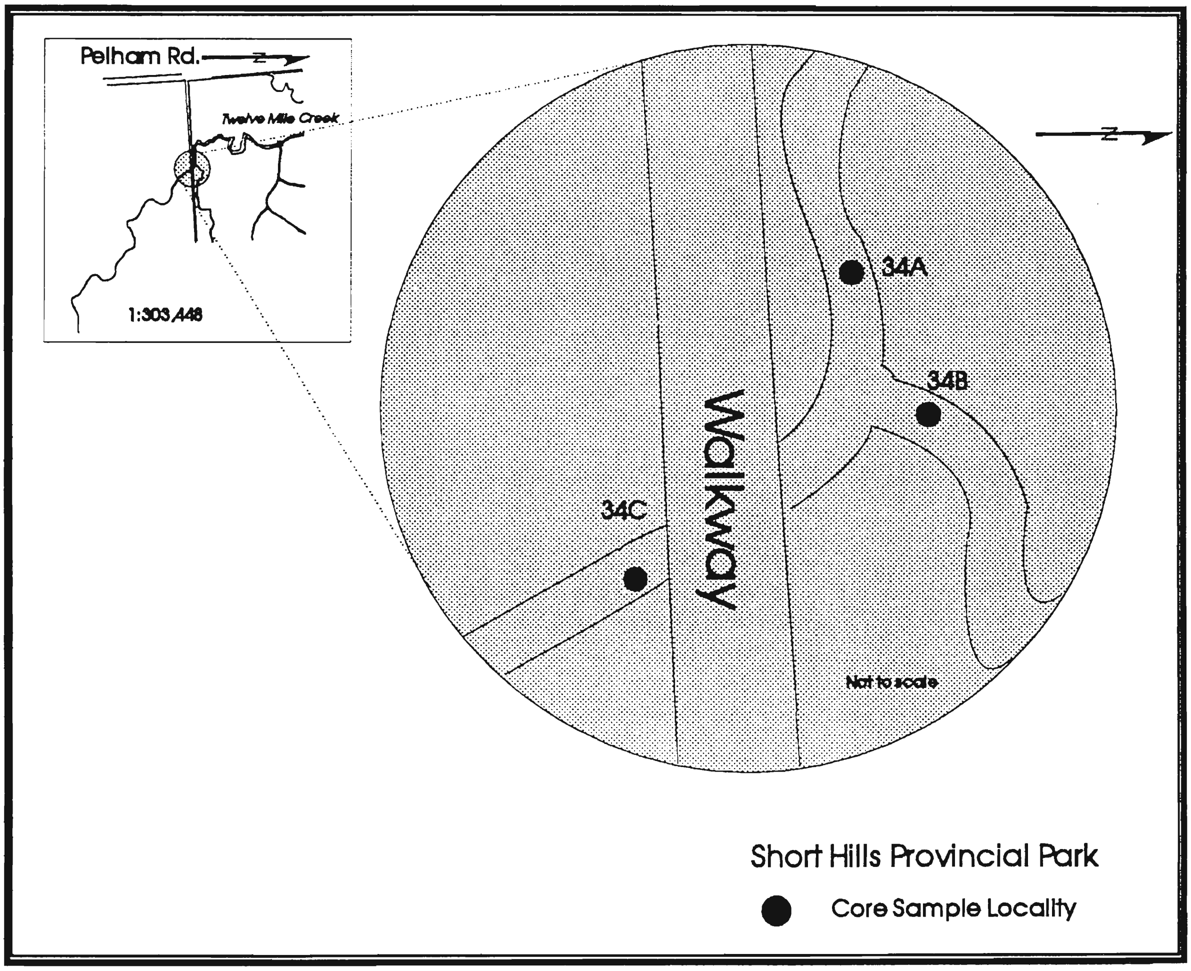


Figure 3: Locality map of Short Hills Provincial Park
Showing sampling stations 34A, 34B, and 34C.

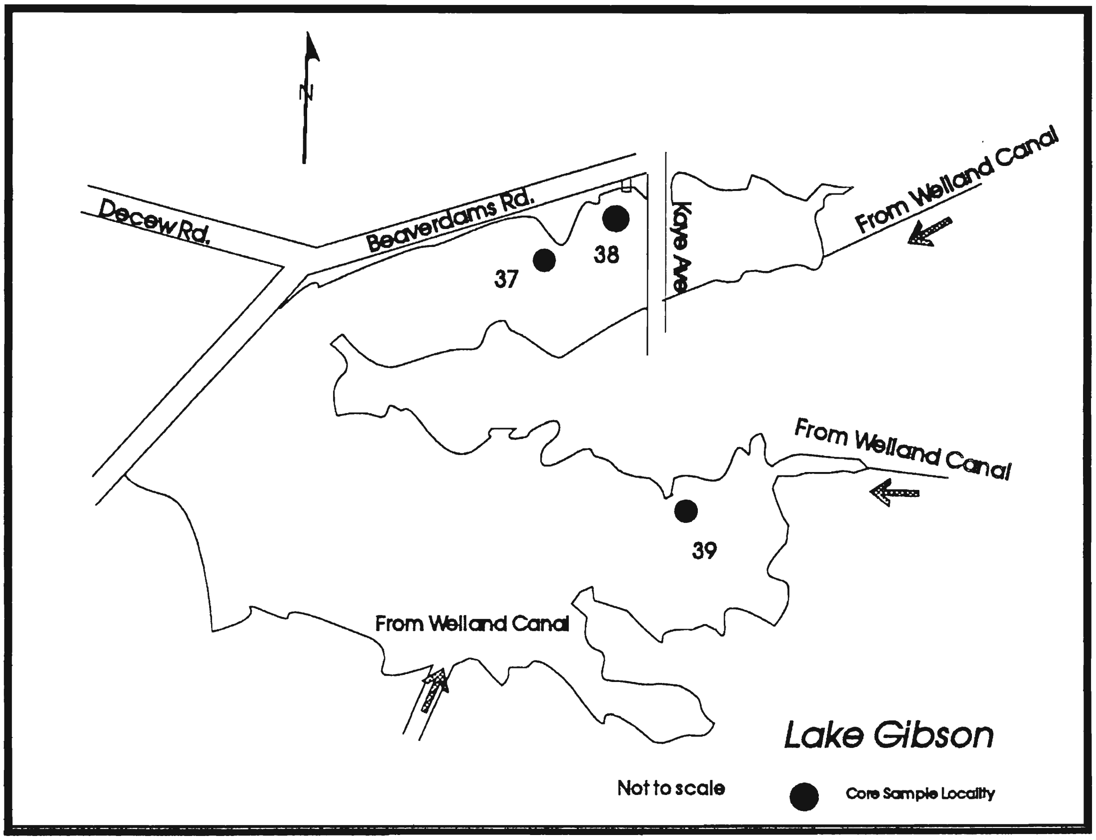
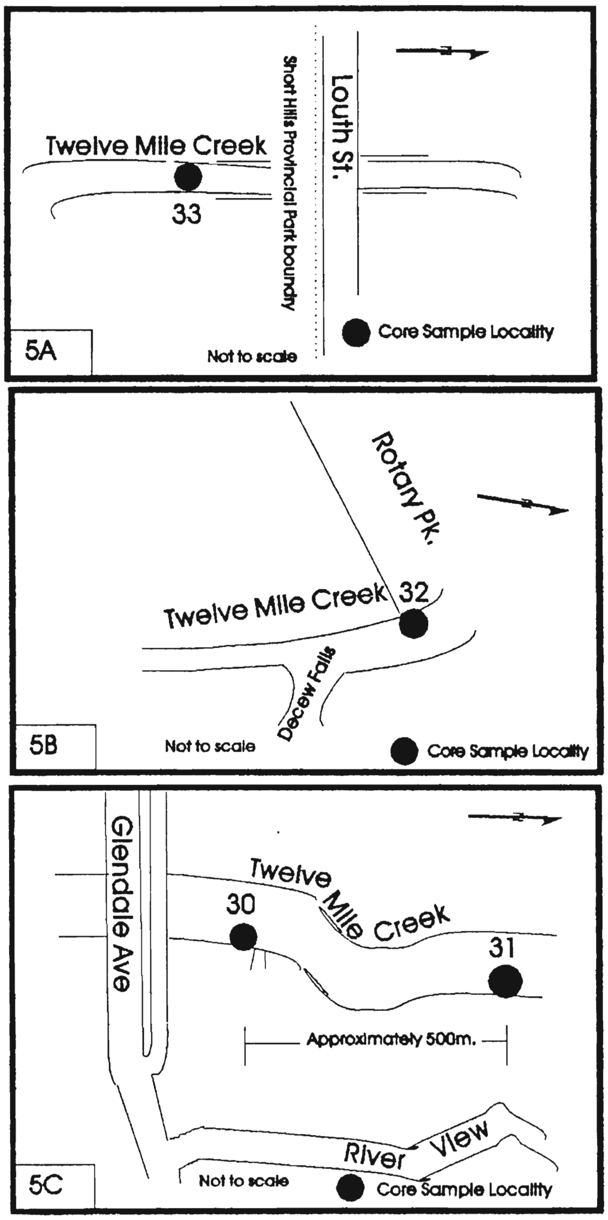


Figure 4: Locality map of the east side of Lake Gibson
Showing sampling stations 37, 38, and 39.

Twelve Mile Creek. Figures 5A, 5B, and 5C show the localities of the sediment cores in Twelve Mile Creek (TMC). Core 33, from just within SHPP off Louth Street, was not analyzed for TPH. The next sediment core (core 32, Figure 5B) was obtained in TMC on the shore of Rotary Park (< 14 mg/kg). Cores 30 and 31 were obtained just downstream from the Glendale Avenue bridge (Figure 5C). Core 30 (< 14 - 173 mg/kg) was obtained from just above the storm outfall, whereas core 31 (< 14 mg/kg) was approximately 500 m downstream from the previous one. TPH values in the sediments of TMC, from below Decew Falls and Glendale Avenue, are well below the Provincial guideline.

Six cores were obtained from the Old Welland Canal and some of its tributaries before they empty into TMC (Figure 6). Cores 20, 19, and WK3 were sampled directly in the Old Welland Canal, whereas cores IC1, IC3, and WK2 came from tributaries emptying into the canal system. The two cores (WK2, 373 - 661 mg/kg; IC3, < 14 mg/kg) draining a golf course have TPH values well below the Provincial guideline. The TPH value of sediments from the other tributary is just below the guideline (IC1, 1122 mg/kg). Of the three samples obtained from the canal, two of them exceed the guideline with 1860 - 4270 mg/kg (WK3) and 5542 mg/kg (core 19), while the third sample (core 20) is low with 556 mg/kg. Since core sample 20 is downstream from samples WK3, IC1, and 19, flow and/or sediment parameters may explain the low TPH value measured at this locality.

Another set of samples from TMC came from upstream of the confluence with the waters of the Old Welland Canal (cores 28 and 29, Figure 7), and another suite of three samples were taken from the canal below Highway 406 (core 26 and 27; Figure 7).The two samples upstream from the canal are low in TPH content (core 28, 53 mg/kg; core 29, 372



Figures 5A, 5B, and 5C: Locality maps of Twelve Mile Creek in the areas of sites 33, 32, 30, and 31(5A, 5B, and 5C follow downstream direction)

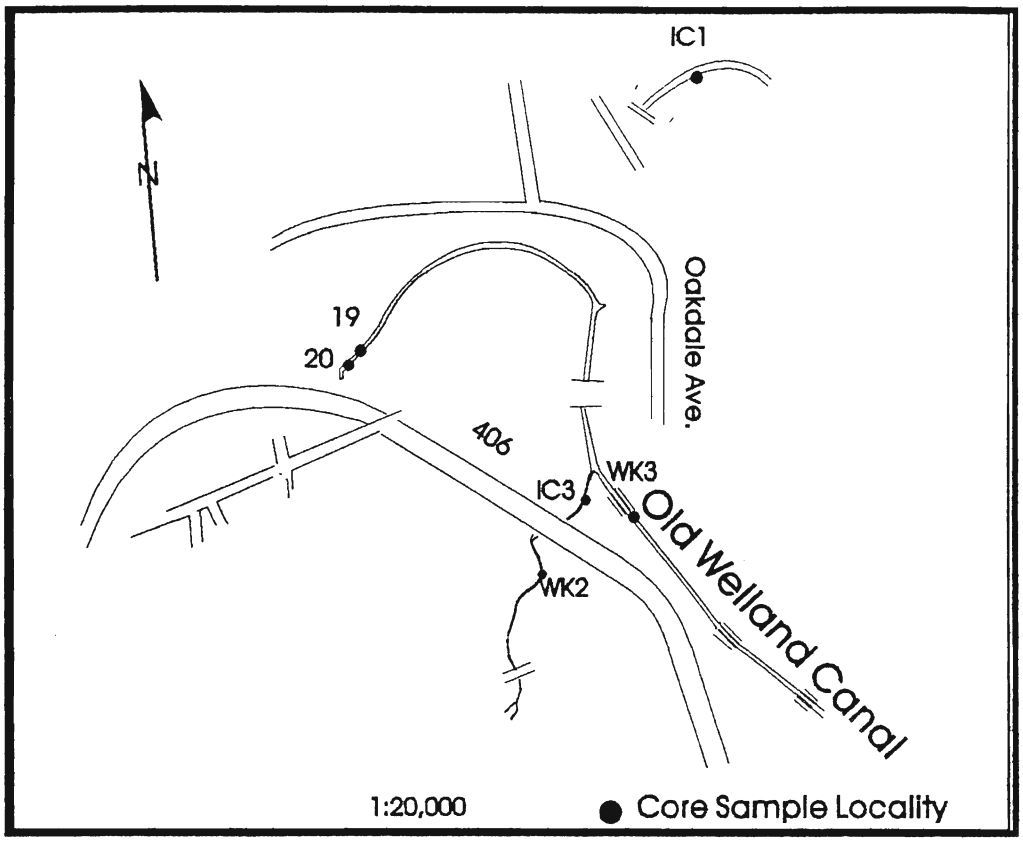


Figure 6: Locality map of the Old Welland Canal and tributaries showing sampling stations WK2, IC3, WK3, IC1, 19 and 20.

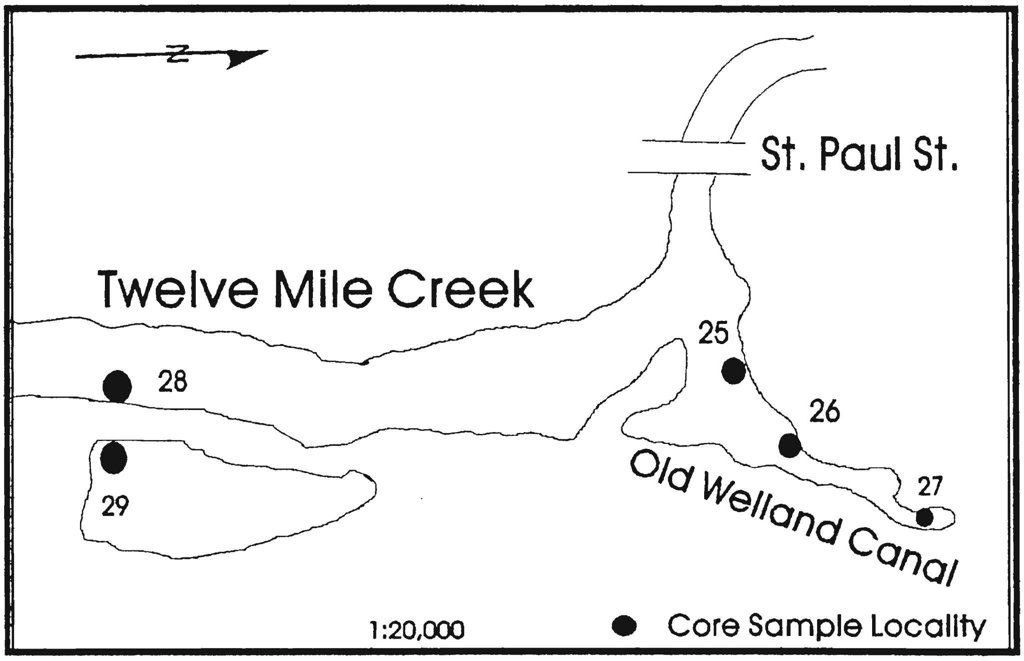


Figure 7: Locality map of Twelve Mile Creek and the terminus of the Old Welland Canal showing sampling stations 25, 26, 27, 28, and 29.

mg/kg), and well below the Provincial guideline. In contrast, the three samples at the confluence of TMC and the Old Welland Canal all exceed the Provincial guideline (core 27, 4316 - 4438 mg/kg; core 26, 626 - 3008 mg/kg; core 25, 2675 mg/kg). It appears that there is a gradual decrease in TPH in sediments downstream in the cutoff branch of the canal (Figure 7).

A set of four samples (cores) were obtained from TMC behind the Hotel Dieu Hospital and adjacent to the St. Catharines Campus of Niagara College (Figure 8). These are downstream from the confluence of TMC and the Old Welland Canal. TPH values in these samples (core 24, 117 mg/kg; core 23, 938 mg/kg; core 1cr, < 14 - 30 mg/kg; core 2cr, < 14 - 228 mg/kg) are all well below the Provincial guideline of 1500 mg/kg.

The last set of cores in TMC were obtained from the creek bed and wetlands just south of the QEW (Figure 9). The two cores just upstream from the wetlands exhibit TPH values just below the Provincial guideline (core B, 567 - 1180 mg/kg; core C, 14 - 1461 mg/kg). Core sample 21, well within the wetland, has a TPH value of 387 mg/kg, which is well below the guideline. In contrast, the two samples at the open end of the wetland area exhibit elevated TPH values. Core sample A has TPH values ranging from 558 to 1560 mg/kg, whereas core 22 sediment contains TPH of 2763 to 3708 mg/kg.

Martindale Pond. A total of seven cores (O1, D1, 2, 4, 5, 6, 7) were obtained from Martindale Pond (Figure 10) and tested for TPH. The TPH contents in these sediments, in many cases, exceeds the Provincial guideline of 1500 mg/kg. Values range from a low of 252 mg/kg at a depth of 4 - 5 cm in core 5, to a high of 5971 mg/kg at a depth of 9 - 11 cm in

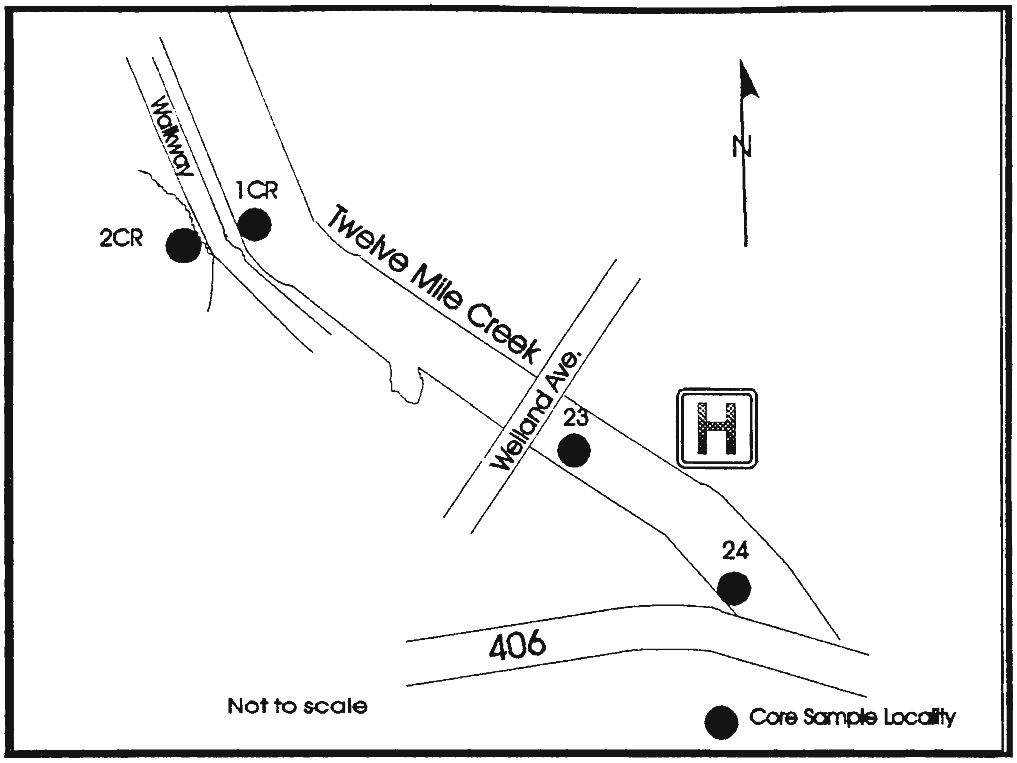


Figure 8: Locality map of Twelve Mile Creek showing sampling stations 23, 24, 1CR, and 2CR.

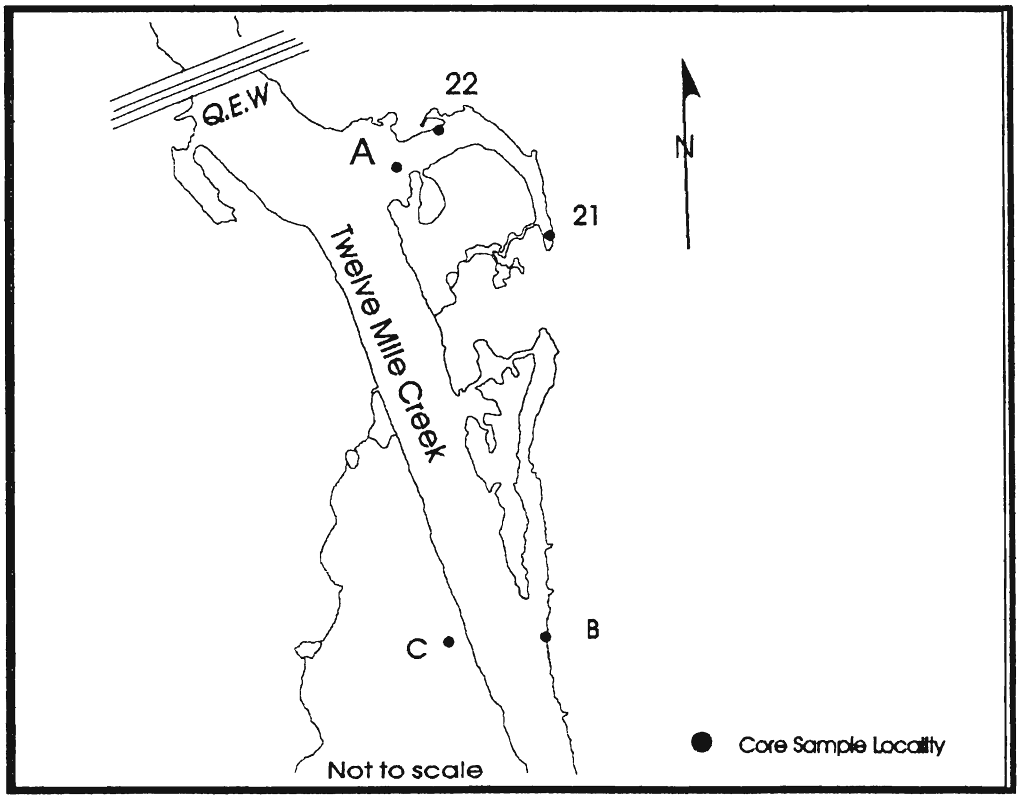


Figure 9: Locality map of Twelve Mile Creek showing sampling stations A, B, C, 21, and 22.

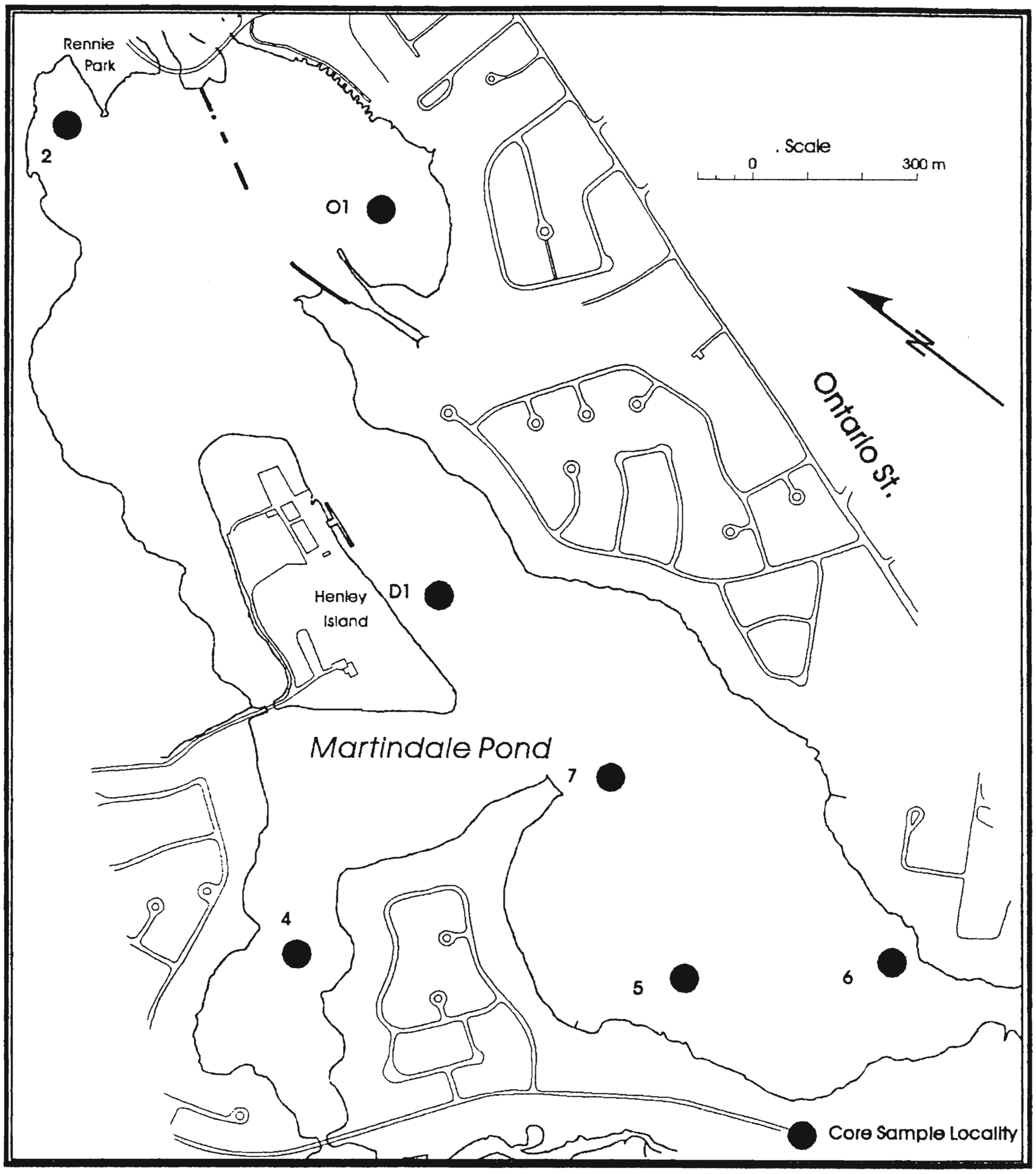


Figure 10: Locality map of Martindale Pond showing sampling sites 2, 4, 5
6, 7, D1, O1.

core 6. Other low values (< 1500 mg/kg) were encountered at sites O1 (33 - 34 cm), 7 (41 - 42.5 cm), 2 (0 - 2 cm), 6 (63 - 65 cm), D1 (8.5 - 10 and 61 - 62 cm), and 5 (4 - 5 and 79 - 81 cm; Appendix 1). High TPH values range from 1942 - 2680 (site O1), 1646 - 2800 (site 7), 2758 - 4491 (site 2), 1883 (site 4), 4478 - 5971 (site 6), 1985 (site D1), and 1463 - 1737 (site 5) mg/kg (Appendix 1).

Metal Fractions

Total Metal Fractions. Total metal concentrations are useful in determining areas of high elemental loading, and may be used to locate point sources. However, speciation and complexation information can not be determined from total metal concentration. It would be advantageous to have such information when doing environmental work, but this was not within the scope of this work, nor is it currently mandated by government guidelines. Total metal contents of sediments will be presented with respect to provincial guidelines and our guidelines (see **Introduction** and **Methods**) to evaluate and assess their environmental status.

Se in sediments is not regulated by the provincial MOEE nor Environment Canada. Although Se concentrations were determined, they are not discussed beyond being recorded in the appendix. The total metal contents in sediments from Jeanette's Creek (Lake St. Clair) and from the modern Welland Canal (core 35) are listed for completeness in the appendix. Total metal values in sediments from the various localities of the TMC watershed in relation to ASQG (Persaud *et al.*, 1992) are listed in Table 3.

Table 3. Total Metal Levels (ppm; Persaud *et al.*, 1992) in sediments of Twelve Mile Creek, Lake Gibson and Martindale Pond.

	Ni	Cu	Cr	Cd	Pb	Zn	As	Al*
LEL	16	16	26	0.6	31	120	6	46000
SEL	75	110	110	10	250	820	33	92000
Locality cores								
Short Hills P. Park								
34A	*40.1*	*26.7*	*64.5*	*0.6220*	13.39	78.7	3.52	41543
34B	*63.9*	*25.3*	*59.7*	0.0724	13.06	81.1	3.06	35872
34C	*41.4*	*24.3*	*61.4*	0.3129	15.57	66.4	*15.51*	*55905*
Lake Gibson								
37	*56.1*	*37.7*	*67.8*	0.1595	*49.84*	*120.9*	*15.29*	*46987*
38	*56.2*	*49.8*	*77.0*	0.1191	*41.97*	*127.9*	*12.07*	*58020*
39	***631.3***	***4267.6***	***1161.4***	***13.76***	***4275.03***	***10971.7***	***83.01***	*47674*
Twelve Mile Creek								
33	*62.4*	*26.1*	*96.7*	*1.2647*	16.15	85.1	5.86	44500
32	*27.8*	*27.8*	*59.5*	0.3078	7.87	104.1	*6.17*	*62383*
31	*29.5*	*25.9*	*60.1*	*0.6627*	12.46	72.4	4.66	43377
30	*54.9*	*27.7*	*62.7*	*0.8786*	12.40	77.2	*9.24*	*48777*
29	*38.8*	*25.8*	*75.7*	<0.0096	9.48	71.3	5.94	*62359*
28	*42.0*	*33.9*	*69.5*	*0.9655*	29.73	112.8	*29.26*	*51691*
27[a]	*48.6*	***456.7***	*105.5*	0.5017	*217.05*	*305.3*	*11.19*	*51763*
26[a]	*58.9*	***239.6***	*77.2*	*0.6033*	*70.05*	*211.1*	***33.63***	*60428*
25[b]	***154.5***	***188.7***	***147.2***	*0.9297*	23.16	*142.0*	*9.81*	*62613*
24	*47.5*	*33.6*	*65.9*	0.2544	22.88	118.5	*7.46*	40563
23	*56.6*	*80.1*	***158.2***	*0.8794*	*74.93*	*232.4*	*16.00*	*51631*
22	***101.2***	*94.7*	*95.3*	*6.4363*	*80.56*	*165.4*	***47.84***	41073
21	*35.3*	*40.4*	*84.5*	<0.0096	*76.00*	82.8	***49.37***	*54093*
1cr[c]	*41*	*38*	*78*	---	*32*	92	N.D.	---
2cr[c]	***103***	*33*	*52*	---	*86*	*168*	N.D.	---
A	***88.5***	*57.9*	*61.3*	*1.4656*	*58.23*	112.8	5.66	*57514*
B	*33.7*	*53.6*	*59.7*	*1.2213*	*80.32*	100.7	*8.50*	*54751*
C	***103.8***	*47.4*	*57.1*	*1.5114*	*44.59*	85.3	*10.71*	*56660*
Martindale Pond								
D1	***89.6***	*50.5*	*78.0*	*1.4030*	*42.70*	*251.2*	***62.97***	*49501*
2	***128.4***	*51.9*	*78.3*	*1.4939*	***984.16***	*280.4*	***49.54***	*74329*
O1	*51.0*	*41.8*	*45.9*	*0.7708*	18.67	*124.6*	*13.67*	*49895*
4	***76.1***	*36.5*	*64.9*	*0.8489*	28.92	*153.3*	*18.91*	*75434*
5	***132.2***	*50.7*	*45.2*	*2.0516*	*34.19*	*205.0*	***62.57***	45066
6	***175.4***	*104.7*	*69.9*	*3.0605*	*119.12*	*228.5*	*9.25*	*52181*
7	***98.0***	*37.2*	*53.9*	*1.8959*	*41.99*	108.5	*9.60*	*47956*

Note: Normal font - below LEL (lower effect level), Italic and underlined font - between LEL and SEL (severe effect level), Bold and italic - above SEL. See Appendix 1 for sediment depth. [a] Old Welland Canal. [b] Old Welland Canal/Twelve Mile Creek. [c] Rowan (1995). *Al guideline values are set in the current study.

Exchangeable Metal Fraction. The exchangeable metal fraction was only determined for selected samples and for metals that did not require graphite furnace analysis. The exchangeable fraction was determined using the first step of Tessier's Selective Extraction Method (1979). Loosely adsorbed metals were exchanged with Mg^{2+} which was deemed indicative of available metals from the sediments. Table 4 lists exchangeable metal values in sediments of the TMC watershed in relation to fresh water aquatic life guidelines set by CCME (1991).

Short Hills Provincial Park. Cores 34A, 34B, and 34C were obtained inside Short Hills Provincial Park (Figure 3) and were tested primarily to set background values for the watershed. Table 3 describes the total Ni, Cu, Cr, Cd, Pb, Zn, As and Al contents. Each of the three cores show that the two tributaries carry sediments with concentrations above the LEL limits. The As levels are above the LEL for core 34C. Sediments from cores 34A and 35B have normal background levels at the no effect level (NEL). Core 34A representing the contribution from the two tributaries, had Cd values greater than the LEL. Sediments from core 34C had Cd values (Table 3) an order of magnitude greater than Cd sediment values from core 34B. Total Pb concentrations in all sediments sampled from Short Hills Provincial Park were below the LEL.

Only core 34A from Short Hills Provincial Park was tested for exchangeable metals (Table 4) since it is a composite of waters from the tributaries of cores 34C and 34B. All exchangeable metals tested were in the acceptable range (below the lower limit; CCME, 1991).

Table 4. Exchangeable metal levels and upper and lower limits (ppm) of CCME (1991) criteria for fresh water aquatic life in sediments of Twelve Mile Creek, Lake Gibson and Martindale Pond.

	Pb	Cr	Cu	Cd	Al	Ni
Lower limit	0.001	0.002	0.002	0.0002	0.005	0.025
Upper limit	0.007	0.02	0.004	0.0018	0.1	0.15
Locality cores						
Short Hills P. Park						
34A	<0.003	<0.006	<0.007	<0.0017	<0.08	<0.026
Lake Gibson						
37	***0.175***	<0.006	<0.007	<0.0017	<0.08	<0.026
38	***0.250***	<0.006	<0.007	<0.0017	<0.08	<0.026
Twelve Mile Creek						
33	***0.214***	<0.006	<0.007	***0.0076***	<0.08	<0.026
32	***0.367***	<0.006	<0.007	<0.0017	***2.64***	<0.026
31	***0.125***	<0.006	***0.242***	<0.0017	***1.01***	<0.026
30	***0.393***	***0.136***	***0.123***	***0.0732***	***0.13***	<0.026
28	***0.060***	<0.006	***0.238***	***0.2176***	***0.51***	<0.026
26	***0.337***	<0.006	***1.544***	***0.0857***	<0.08	<0.026
24	***0.077***	<0.006	***0.163***	***0.0890***	<0.08	<0.026
23	***0.120***	<0.006	***0.481***	***0.1960***	***0.99***	<0.026
22	***0.451***	***0.062***	***0.554***	***2.2833***	***0.23***	***3.04***
21	***0.294***	***0.123***	***0.370***	***0.4626***	***0.21***	<0.026
A	***0.310***	***0.041***	***0.295***	***0.5370***	***1.64***	***1.17***
B	***0.191***	<0.006	***0.441***	***0.0734***	***0.61***	<0.026
C	***0.184***	<0.006	***0.718***	***0.3275***	***0.24***	***7.27***
Martindale Pond						
D1	***0.311***	<0.006	***0.759***	***0.8587***	***2.49***	***2.99***
2	***1.307***	<0.006	***1.268***	***0.9172***	***4.99***	***4.17***
O1	***0.200***	<0.006	***0.589***	***0.2552***	***1.80***	<0.026
4	***0.358***	<0.006	***0.513***	***0.2266***	***1.07***	***0.48***
5	***0.293***	<0.006	***1.326***	***1.0215***	***1.97***	***16.31***
6	***1.312***	<0.006	***1.158***	***0.9582***	***1.35***	***9.82***
7	***0.197***	***0.090***	***0.396***	***0.4394***	<0.08	***2.85***

Note: Normal font - below lower limit, underlined font- between lower and upper limits, bold font - above upper limits (CCME, 1991). See Appendix 1 for sediment depths.

Lake Gibson. As mentioned in the TPH section, core 39 in the south end of Lake Gibson, has a different source than cores 38 and 37 which are located in the north section of Lake Gibson (Figure 4). Sediments from cores 39, 38 and 37 have high total Ni concentrations near the surface (Table 3). Core 39 sediments exceed the SEL Ni guideline, while the Ni values were between LEL and SEL levels for cores 38 and 37. A similar trend was found for total metal concentrations of Cu, Cr, Pb, Zn and As. Total Al was above background levels for each of the cores and thus marked above LEL. Total Cd concentrations varied between cores 37, 38 and core 39. Core 39 had Cd values exceeding SEL, in the other two cores Cd was in the normal background level range.

Of the three cores sampled in Lake Gibson, only sediments from cores 37 and 38 from the north end of Lake Gibson, were analysed for exchangeable metals (Table 4), and showed low levels (below the lower limit; CCME, 1991) for Cr, Cu, Cd, Al, and Ni. Exchangeable Pb was above upper limit levels in these two cores.

Twelve Mile Creek. Data in Table 3 show that Twelve Mile Creek sediments just south of Louth Street (core 33), Decew Falls (core 32) and Glendale Avenue (cores 30 and 31) have total Ni, Cu, and Cr contents above the LEL. Total Cd values for this area are in excess of the LEL in SHPP (core 33) and downstream of Glendale Avenue (cores 30 and 31). Relatively low Cd concentrations, below the LEL, were found just below Decew Falls (Core 32). Total Pb and Zn concentrations were all below the LEL (Table 3). Total As and Al values exceeding the LEL were found in cores 32 and 30 which are closest to Decew Falls and Glendale Avenue, respectively, while cores 33 and 31 upstream and downstream of this area had concentrations below the LEL.

Exchangeable Ni in sediments from cores 30 to 33 of the Twelve Mile Creek at Louth Street, Decew Falls, and Glendale Avenue (Table 4; Figures 5A, 5B, and 5C) was below the mean detection limit and are thus considered to be well below the lower limit (CCME, 1991). High exchangeable Cu, in excess of the upper limit, was found downstream of Glendale Avenue (cores 30 and 31), while Cu in sediments of upstream cores 32 and 33 were below the lower limit. Core 30 had available Cr above upper limit, while core 31, which is downstream, had levels below the lower limit. This may reflect differential sewer loadings along the creek. Exchangeable Cr in sediments from upstream cores 32 and 33 were also below the lower limit. Sediments from cores 32, 31, and 30 which are downstream of Decew Falls have exchangeable Al concentrations above the upper limit, while upstream values for core 33 were below the mean detection limit (MDL; i.e., below the lower limit). Exchangeable Pb in cores 30 to 33 were all above the upper limit. Exchangeable Cd exhibited trends in cores 30 to 33 similar to those exhibited by the total metal contents.

Old Welland Canal sediments, south of the QEW (Figure 1) were tested only for TPH, thus the Twelve Mile Creek and Old Welland Canal sites (Figure 6), are discussed as one set because one can not be sure where the mixing zone lies. Core 29 was advanced in an abandoned channel, a cut-off meander of the creek, which is connected through a culvert with the main channel (Figure 7).

Cores from Twelve Mile Creek, in the vicinity of Old Welland Canal, (Figure 7) 29, 28, 27, 26 and 25 have total Al (Table 3) above background level (LEL). Total Cd exceeds the LEL in cores representing both the creek and the Old Welland Canal section (28, 26, and 25). Values below LEL were found in cores 27 and 29. Total Cr and Ni concentrations for both areas were relatively high, and all were above the LEL, with those in core 25 in excess of the SEL. Total Cu values demontrate a clear distinction between the creek and the Old Welland Canal. Sediments from cores 28 and 29 have levels above the LEL, while cores 25, 26, and 27 have values well above the SEL. Total Pb exceeds the LEL in the Old Welland Canal section (cores 26 and 27). Cores 25, 28 and 29 which represent both areas were found to have Pb levels below the LEL. Total Zn exceeds the LEL in only those cores representing the Old Welland Canal section while upstream Twelve Mile Creek core sediments 28 and 29 have values below the LEL. Total As concentrations exceed the LEL for cores 27 and 28 while core 26 exceeds the SEL and core 29 was below the LEL.

Only cores 28 and 26 from the Twelve Mile Creek in the Old Welland Canal vicinity (Figure 7) were tested for their exchangeable metals (Table 4). These sites were considered to be representative of their immediate areas. Core 28 had exchangeable Al concentrations that exceeded the upper limit, and core 26 had concentrations near background levels (i.e., below MDL). Exchangeable Cd concentrations exceeded the upper limit (CCME, 1991), while exchangeable Cr and Ni were below the MDL. Exchangeable Cu and Pb exceed the upper limits, with considerably higher concentrations in core 26.

Figure 8 depicts the Twelve Mile Creek in the vicinity of the Hotel Dieu Hospital. Data of cores 1cr and 2cr were obtained from C. Rowans B.Sc. Thesis (1995; by permission). Using the hospital as a reference point, it was observed that total Pb concentration (Table 3) increased downstream of the hospital. Total lead in cores 1cr, 2cr and 23 are above the LEL, while core 24, upstream of the hospital, was found to have near background levels (below LEL). Total Cu concentrations for cores 1cr, 2cr, 23 and 24 were above the LEL.

Downstream of Welland Avenue, Cr in sediments from cores 1cr and 2cr were above the LEL. Upstream of the hospital and adjacent to Highway 406, Cr in core 24 was above the LEL, while on the immediate downstream side of the hospital, Cr in core 23 was above the SEL. Total Cd was found to be elevated downstream of the hospital (core 23, above LEL), while upstream, core 24 had values near background levels (below LEL). Total Al content was above LEL (set in this work) levels in core 23 and below the LEL in core 24. Total Ni concentrations for cores 24, 23, and 1cr were above the LEL, and in core 2cr it was above the SEL. Total Zn was found elevated above the LEL at core sites 2cr and 23, while in cores 24 and 1cr it was below the LEL. Total As concentrations, tested in core samples 23 and 24, were above the LEL.

Exchangeable Pb, Cu and Cd concentrations (Table 4) were above the upper limit (CCME, 1991) in cores 23 and 24, with the downstream core 23 values being much higher than those upstream of the hospital (core 24, Figure 8). Exchangeable Cr and Ni fractions for both cores were found to be at background levels, well below the lower limit. Exchangeable Al concentrations at core site 24 were below MDL (i.e., below lower limit), while downstream at core 23, Al was above the upper limit.

Near the terminus of Twelve Mile Creek is an abandoned meander, downstream of General Motors and immediately upstream of Martindale Pond, in which five cores were advanced (cores 22, 21, A, B and C, Figure 9). Total Cu, Cr, Pb and Al for all five cores had values above the LEL (Table 3). With the exception of core 21, all other sample sites had total Cd values that exceeded the LEL (Table 3). Total Ni concentrations were above the LEL at core sites B and 21 while cores C, A, and 22 were above the SEL. Total Zn was below the LEL with the exception of site 22. Total As concentrations were above the SEL at sites 22 and 21, and above the LEL for upstream cores B and C; a low anomaly was found at site A (below LEL).

Exchangeable metal fractions were obtained from core sediments, 22, 21, A, B and C, within the abandoned meander (Table 4, Figure 9). Exchangeable Pb, Cu, Cd, and Al in each of the cores were above the upper limit (CCME, 1991). Exchangeable Cr concentrations were above the upper limit in cores A, 22, and 21. Upstream cores B and C had levels below the MDL (background levels; i.e., below lower limit). Exchangeable Ni was above the upper limit at sites C, A, and 22, while in cores B and 21 they were below the MDL (lower limit).

Martindale Pond. Figure 10 depicts the sampling sites in Martindale Pond (cores D1, 2, O1, 4, 5, 6 and 7). Ni in sediments from core O1 exceed the total LEL, while total Ni in the other cores exceeds the SEL. Total Cu, Cr, Cd, Zn and Al values exceed the LEL guideline for all cores with the exception of core 7 whose total Zn is just below the LEL. Total Pb is below the LEL in cores O1 and 4, above the LEL in cores 6, 5, 7 and D1, and above the SEL in core 2. Total As was highly variable in the cores from the pond. Three sites (5, D1, 2) had As contents above the SEL, and in four sites (6, 7, 4, O1) they were above the LEL.

Every sediment sample from Martindale Pond was tested for exchangeable metal. All samples had exchangeable Pb, Cu and Cd above the upper limit (CCME, 1991). Exchangeable Cr was below the lower limit with the exception of those from core 7 which were above the upper limit. Exchangeable Al exceeds the upper limit in all cores, except core

7, where it was below the Al MDL. Core sites 5 and 6, closest to the mouth of Twelve Mile Creek, had much higher Ni values than any other Martindale Pond site.

DISCUSSION

Water Quality

Water quality readings at the studied sites are uniquely different and as such reflect differential sources of anthropogenic impact on the Twelve Mile Creek watershed. The headwaters of the Twelve Mile Creek within Short Hills Provincial Park probably reflect conditions most indicative of its former natural state. Water quality parameters throughout the remaining segments of the creek are greatly influenced by its anthropogenic use.

Total Petroleum Hydrocarbons

Not all samples could be tested; therefore, it is advised that more TPH work be done in the Twelve Mile Creek watershed. Areas directly related to recent or past industrial activities were found, using TPH (a subset of O&G; see **Results**), to exceed the O&G guidelines. In particular, sample sites directly related to the Welland Canal, such as the Old Welland Canal (Figures 6 and 7) and the south side of Lake Gibson (core 39, Figure 4) have very high values. The area just upstream of the QEW (Figure 9) shows increasing values with distance downstream (Appendix 1), which may be attributed to past shipping activities or industrial and combined sewer discharges into the creek (Figures 1 and 2).

Martindale Pond core sediments are above the TPH (O&G) sediment guideline. The highest TPH values for the cores sampled in Martindale Pond are depicted in Figure 11, and were found generally to be above the O&G (CCME, 1991) guideline. Large variation between the cores adjacent to each other suggests localization of TPH near the point source or in areas of favourable sediment conditions. This is likely a combination of past boating activities, combined and industrial sewer discharge, and sediment-type contributions from Twelve Mile Creek. Although only one core (4) was tested near Richardson's Creek, it is an unlikely source for TPH since the sewer maps (Figures 1 and 2) show no industrial or combined sewer discharges into the creek.

Similar organic screening tests were conducted by Canadian Henley Rowing Club (CHRC, 1995) and Public Works and Government Services Canada (PWGSC, 1994). High O&G values were found by PWGSC in sediments (> 2000 mg/kg) sampled near core sites O1 and 2. Sediments sampled near core sites D1, 7, 4, 5, and 6 had TPH values well below the 1500 mg/kg guideline. CHRC reported 1500 mg/kg of O&G in sediments at 135 to 155 cm depth in one core only. Otherwise, TPH results of this work sharply contrast with those found by CHRC. At site 2, values from the surface to 40 cm depth range from 793 to 4,491 mg/kg, while CHRC reported 20 mg/kg for the 30 to 35 cm interval. In addition, CHRC reported 1,000 mg/kg (0 - 20 cm depths) of O&G, while the current study found TPH levels of 2800 and 1646 mg/kg for depths 13 - 15 and 22 - 25 cm, respectively. The greatest TPH values found in the pond were at the mouth of Twelve Mile Creek (core 6) with TPH values as high as 5971 mg/kg. This clearly is higher than the values reported by PWGSC for this area (average 100 mg/kg of O&G). Core A, immediately upstream of Martindale Pond, (Figure 9) had TPH values of 1560 and 558 mg/kg for the 2 - 8 cm and 25.5 - 28 cm intervals, respectively, while CHRC reported values of 40 mg/kg of TPH at 5 -15 cm near this site.

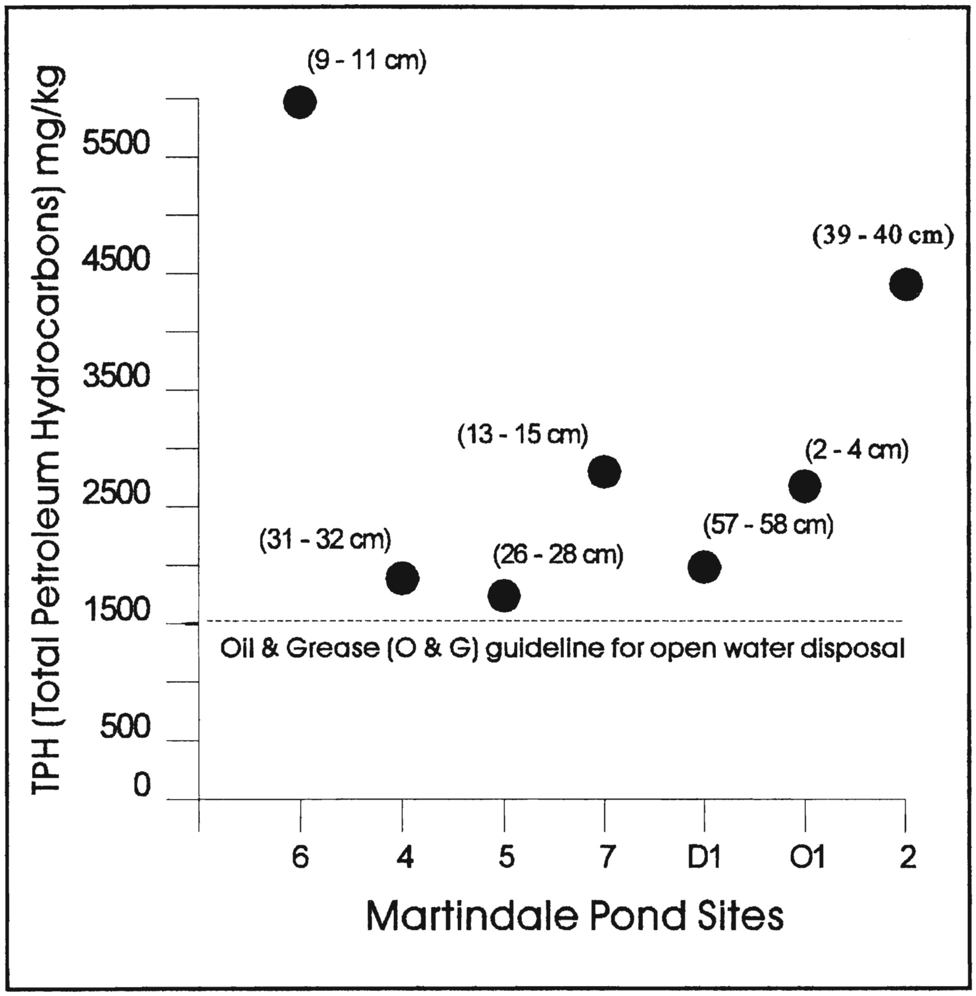


Figure 11: Highest TPH (Total Petroleum Hydrocarbons) of core sediments from Martindale Pond with labelled sediment depths in relation to the CCME guidelines for open water disposal (Oil & Grease guideline = 1500 mg/kg)
Note: Sites are plotted in the downstream direction, with sites 6 and 4 from opposite upstream tributaries to Martindale Pond.

Old Welland Canal results support the TPH values found in Martindale Pond. Although there are vast differences in the anthropogenic loading of organic compounds between this work and others, this work agrees more closely with the PWGSC report than with the CHRC report. The areas of high TPH (O&G) values (greater than the guidelines), in particular those with good control (the Old Welland Canal and Martindale Pond) have sediments which according to the Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario (Persaud *et al.*, 1992) are not fit for open water disposal and accordingly should be treated as hazardous material.

Total and Exchangeable Metal Fractions

Discussions and interpretations of watershed point sources are possible due to the various tributaries along the Twelve Mile Creek, including points of sewer discharge, contributing to the sediments heavy metal content. However, caution must be exercised when interpreting such data because of the physical properties of the creek. The creek is engineered to a maximum width of 30 to 50 m. In comparison to naturally evolved streams, Twelve Mile Creek does not meander, and is fairly straight. Large volumes of water are carried downstream to Martindale Pond. This is very important when considering laminar and vertical mixing gradients. Due to the velocity of flow, sediment metal loading from outfalls may be horizontally limited and result in sampling errors (i.e., sampling from the wrong shore). Sampling near the center of the creek bed would probably have been ideal, however safety reasons did not permit this. In addition, since the majority of the cores were sampled from shore access, it is possible that erosion slumping may have contributed to the sediment column in the cores.

Recent work published on the Twelve Mile Creek watershed has primarily dealt with Martindale Pond. The Martindale Pond Property Transfer Assessment Report was prepared for PWGSC (September 1994) and another recent study was prepared for the CHRC (December 1994). Both works were contracted out to private environmental consultants, referred to here as Consultant 1 and Consultant 2, respectively. Although both consultants tested for total metal content in the sampled sediments, their testing procedures varied significantly. Consultant 1 used homogenized core sediments to obtain representative metal values of each core. Consultant 2 generally sampled selective horizons, which were generally 10 - 15 cm thick. Both testing procedures, although acceptable to the government agencies involved, have obvious and inherent scientific errors. The PWGSC consultant's (#1) method diluted sediments of high contaminant loading by homogenization and the CHRC consultant (#2) may have overlooked sediments of high contaminant loading by testing only a few selective horizons. Their sampling strategies contrast sharply with the approach of continuous and selective horizon sampling and analysis, which from a scientific viewpoint should provide more insight into anthropogenic impacts on TMC watershed sediments over time. Since the MOEE does not require exchangeable metal fraction information neither consultants reported it. Exchangeable metal fraction concentrations are at least two orders of magnitude less than their total metal counterparts, thus, supporting Tessier's *et al.* (1979) observation that the majority of metal fractions are tightly bonded.

Total Ni concentrations generally increase downstream in Twelve Mile Creek. Headwater sediments from the Short Hills Provincial Park have metal contents above the LEL, as have other sites downstream. Large values (> SEL) were found in areas closest to storm and combined sewers, sewer outfalls, industrial sewers and waterways associated with the Welland Canal system (Figures 1 and 2). These point sources, particularly the waterways associated with the Welland Canal system, are likely sources of Ni contamination since the system has historically serviced the metal industry. With the exception of core site O1, all sites in Martindale Pond had sediment horizons with total Ni values above the SEL (Table 3). The PWGSC consultant reported that all sediment samples from Martindale Pond had values greater than the LEL, with five sites, located in the north region of Martindale Pond to east of Michael Rennie Park, greater than the SEL. The CHRC consultant (#2) reported values exceeding the SEL from Twelve Mile Creek to Michael Rennie Park. The CHRC report supports the current study in which each site in the pond, including sediments near site 4 (in contrast to the PWGSC report), had Ni values exceeding the SEL, except core site O1. For example, high levels of contamination point to the storm sewer (S14; Figure 2) at Lookout Park (Martindale Pond site) as a point source, and the main contributor to core 4 sediment Ni contents.

Areas tested for exchangeable Ni fraction (Table 4) are below the mean detection limit (lower limit; CCME, 1991) whereas their counterparts (i.e., total metal fractions) were above the LEL (not SEL; Table 3). In contrast, areas sampled adjacent and downstream of sewer outfalls had exchangeable metal contents that greatly exceeded the Ni upper limit (CCME, 1991). It is not unexpected that the exchangeable metal concentration in sediments in cores 39 and 25, both of which are associated with the Welland Canal system, would exceed the guideline. Similarly, all sediments from Martindale Pond tested for available Ni content had values that exceeded the upper limit for sediments whose total metal concentration also exceeded the SEL.

Similar to Ni, total Cu values increased downstream in Twelve Mile Creek from Short Hills Provincial Park and the north side of Lake Gibson to Martindale Pond. Sites adjacent to sewer outfalls and the waterways associated with the Welland Canal system showed elevated total Cu levels. Examples of elevated Cu contents noted near outfalls are cores 23, 22 and C. Unlike total Ni contribution from the outfall near site 30, total Cu was not elevated. High Cu values (> SEL) were localized to waterways that are associated with the Welland Canal system. Martindale Pond sediment Cu values, unlike the Ni values, did not exceed the SEL as was reported by the PWGSC consultant (#1). However, the CHRC study did report Cu values greater than the SEL in Martindale Pond. In particular, a sample less than 50 m from site 2 was reported to have a Cu concentration of 117 ppm (30 - 35 cm). At the same depth in core 2 the determined concentration was 38.9 ppm and the highest value in core 2 (Table 3) was 51.9 ppm. This demonstrates the complexity of the pond's physico-chemical sedimentation patterns. In addition, the highest value found in the pond was at core site 6 near the mouth of Twelve Mile Creek (105 ppm) which is just below the SEL cutoff.

Similar to the exchangeable Ni trends, exchangeable Cu values are more sensitive environmental indicators than are total metal values, and are below the lower limit (CCME, 1991) for headwater sediment samples (Short Hills Provincial Park and north side of Lake Gibson). However, downstream of Glendale Avenue (near sewer outfalls) all sediments had Cu values above the upper limit, including Martindale Pond. Since minimal sampling was done in Lake Gibson, and the highest exchangeable fractions were found in the south side (core site 39 near the Welland Canal) it is interpreted that the Welland Canal is the prime contributor of exchangeable Cu. This is evident in the total Cu of the Old Welland Canal since sediment cores in SHPP had total Cu contents below the LEL, while downstream of

Decew Falls (Lake Moodie and Lake Gibson; waterways associated with the Welland Canal system) sediments had elevated exchangeable Cu.

Total Cd concentrations, similar to Ni and Cu, are elevated near areas of sewer outfalls. Total Cd concentrations in sediments (core 34C) from one of the two tributaries in Short Hills Provincial Park, suggest that the tributary is a large contributor of Cd. In addition, Cd concentrations from sediments sampled in core 33, also within Short Hills Provincial Park, and representing an additional tributary suggest that tributary is also a contributor of total Cd. Most areas sampled have total Cd values greater than the LEL. Low metal contents occur along Twelve Mile Creek and may be due to differential flow characteristics of the fluvial system. Examples of this process are the metal contents in sediments from cores 32 and 29. The former core, just below Decew Falls, is from an area of high water velocity and thus area of reduced sedimentation and contaminant accumulation. In contrast, core 29 from the oxbow pond may represent an area of reduced water flow velocity with greater sedimentation potential, as well as an area of pre-industrial use of the upper reaches of the Twelve Mile Creek. Core 28, which is located slightly upstream from core 29, but within the "modern" engineered segment of the Twelve Mile Creek has higher total Cd levels than the latter (Table 3). The highest Cd concentrations in Twelve Mile Creek were found near a storm sewer outfall at site 22. All sediment cores sampled from Martindale Pond had total Cd with values greater than the LEL. The PWGSC study reported that only 38% of sediments sampled in Martindale Pond had Cd values exceeding the LEL. In particular, cores sampled near sites O1, 2, 4, and 5 were found to greatly exceed the LEL. The CHRC study reported similar concentrations, to this work, for sediments sampled near sites 6, 5, 7, and D1. In contrast to this work, the CHRC study reported sediments near site 2 (30 - 35 cm) as having 0.5 ppm total Cd (< LEL) while this study found total Cd values ranging from 0.88 ppm to 1.05 ppm at depths of 26 - 28 cm and 46 - 47 cm, respectively.

Exchangeable Cd fractions are below the lower limit (CCME, 1991) for core sediments 34A, representing the two southern Twelve Mile Creek tributaries in SHPP. Similar to total Cd, core 33 also in SHPP has exchangeable Cd values above the upper limit. Areas tested below Decew Falls have exchangeable Cd in excess of the upper limit. Areas adjacent to outfalls had large spikes in exchangeable Cd and were on average an order of magnitude greater than upstream sediment samples. The best example of this anomaly is sediment from core 22 with 2.3 ppm of exchangeable Cd which exceeds the total metal LEL sediment guideline established by the MOEE (Persaud *et al.*, 1992).

From the headwaters (SHPP and Lake Gibson) to the terminus of Twelve Mile Creek (Martindale Pond), the majority of sites sampled had total Cr concentrations above the LEL. Three (> SEL) anomalous sites were found. Similar to those of other metals, the Cr anomalies were found in areas directly related to the Welland Canal (core 39 from Lake Gibson and core 25 from Old Welland Canal). Otherwise, core site 23 was the only area close to a city sewer outfall that had Cr values that exceeded the SEL. All cores in Martindale Pond had sediments with total Cr values greater than the LEL. The PWGSC study reported that only 7% of the cores sampled were above the Cr LEL guideline. In addition, sediments sampled near (< 50 m) sites O1, 2, D1, 7, 4, 5, and 6 were reported as having values below the Cr LEL. In contrast, the CHRC study reported that all sediments tested had Cr values greater than the LEL.

The majority of sites tested had exchangeable Cr values below the lower limit (CCME, 1991). Only areas immediately downstream of combined sewer overflows and industrial sewer discharge sites had exchangeable Cr values greater than the upper limit (sites 30, 21, 22, and A).

Total Al did not follow the trends of the previously mentioned metals. Using guidelines set in this work, all areas in the Twelve Mile Creek watershed had sediments that exceeded the LEL. None of the sediments tested had Al greater than the SEL. The waterways associated with the Welland Canal system and sewer outfalls did not contribute greatly to Al loading. Two sites (4 and 2) in Martindale Pond had the greatest values, and the suspected contributor is sediments washed in from Richardson's Creek. This agrees with Rowan's work (1995), who found consistently elevated levels (well above the SEL set in this work) in Richardson's Creek. The high Al values found at site 2 near Michael Rennie Park may be attributed to past shipping activities. This study found, in sediments from core site 7 (13 - 25 cm) that Al concentrations range from 39,754 - 1087 ppm. Similarly, the CHRC study reported concentrations of 23,000 ppm at depth of 10 - 20 cm for sediments near site 7. However, the CHRC study also reported total Al values for core sites 2, D1, 5, and 6, that were 2.5 to 4 times less than those reported in this study for corresponding depths. The PWGSC study did not report total Al values.

Exchangeable Al was below the lower limit (CCME, 1991) for headwater sediment samples. Most sampled areas downstream of Decew Falls had values exceeding the upper limit. It appears that waters from Decew Falls, Old Welland Canal, and Richardson's Creek are the main contributors of exchangeable Al (Table 4) in sediments of the TMC watershed.

The natural headwater area (SHPP) had total Pb values that were at background levels (below LEL), while areas such as Lake Gibson (core 39) and the Old Welland Canal (waterway associated with the Welland Canal system) had sediments with total Pb concentrations that exceeded or were close to the SEL. The sites tested downstream of Decew Falls and upstream of the Old Welland Canal had values less than the LEL. Downstream of sewer outfalls, located just upstream of site 23, all cores sampled had total Pb values greater than the LEL.

Site 2 in Martindale Pond was the only area that had sediment horizons with total Pb fractions greater than the SEL, which may reflect past shipping activities or dredged material deposited from the 1960's. In the PWGSC study, 58% of sediments sampled by Consultant 1 were reported as having total Pb concentrations greater than the LEL. Unlike this study, sediments sampled near (< 50 m) site O1 were reported greater than the LEL. The discrepancy can be reconciled since Consultant 1 sampled to a depth of 68 cm while only 34 cm sampling depth was achieved at site O1. Consultant 2 (CHRC study) did not sample in the area of site O1. The PWGSC study reported total Pb values of 158 ppm (above the LEL) for sediments sampled near site 2 at depths 0 - 56 and 0 - 64 cm (these cores were averaged to obtain the concentration) and the CHRC study also reported concentrations greater than the LEL at depths of 30 - 35 cm. Using data from this work for direct comparison over the same depth horizon, only 26.8 ppm of total Pb (< LEL) was found. However, at greater depths (72 - 82 cm) total Pb concentrations increased from 269 (> SEL) to 984 ppm (>> SEL).

Similar to Cu, Ni, Cd, and Al, the exchangeable Pb fractions proved to be a more sensitive indicator of anthropogenic loading than its total metal content. All exchangeable Pb fractions, except SHPP core 34A which had background level values, were above the upper limit (CCME, 1991). Similar to the total Pb distribution pattern, the waterways associated with the Welland Canal system did contain relatively high levels of exchangeable Pb. In addition, areas downstream of storm, combined overflow, and industrial sewer outfalls, had sediments with exchangeable Pb concentrations that were markedly higher than sediments sampled upstream. Unlike total Pb concentrations, all cores sampled in Martindale Pond had exchangeable Pb concentrations that exceeded the upper limit. Core site 2, similar to total Pb, had sediments with exchangeable Pb concentrations that were an order of magnitude greater than most other areas in the watershed. Core site 6 had sediments with exchangeable Pb concentrations slightly greater than core site 2. This was not found in the total metal analysis, and must be the result of sewer and Welland Canal discharges into Twelve Mile Creek.

Total Zn concentrations were below the LEL for most areas not directly influenced by the Welland Canal or immediately downstream of sewer outfalls. SHPP had total Zn levels below LEL, while those at sample sites 23 and 22 were above the LEL. Both of these sites are immediately downstream of city outfalls. Further downstream, in Martindale Pond, Zn values at the majority of sites exceeded the LEL. Rowan (1995) found that the majority of sediments sampled from Richardson's Creek had Zn concentrations less than the LEL. It is likely that total Zn loading was contributed by the city outfalls along Twelve Mile Creek, with sewer outfalls contributing Zn around Martindale Pond. All cores sampled in Martindale Pond had sediments with total Zn concentrations greater than the LEL except core 7. Consistently high Zn concentration with depth was found in areas of low flow velocity, such as at sites 5, O1, and 2. The PWGSC study reported that 35% of the sampled pond sediments had Zn concentrations greater than the LEL. In addition, Zn in sediments sampled near sites O1 and 2 were greater than the LEL, while those sampled near sites 6, 7, 5, 4 and D1 were less than the total Zn LEL. The CHRC study reported total Zn concentrations in sediments sampled near sites 2, 5, 6, and 7 as being greater than the LEL (Consultant 2 did not sample near sites O1 or 4).

The majority of sample areas in the watershed had total As levels above the LEL. Low concentrations were found in sediments in one of the Twelve Mile Creek headwater tributaries (site 34B). Areas with As SEL exceedances are the waterways connected to the Welland Canal. Sites close to storm, combined and industrial sewer outfalls were above the LEL. Sites 21 and 22, which are close to each other, had sediments with total As concentrations above the SEL, which suggests that the storm sewer outfall at site 22 is a contributor of total As. In Martindale Pond, As values were found to fluctuate from above to below the SEL (core 6 to core 2) in the downstream direction of flow. The linearity and magnitude (2 x SEL cutoff) of the total As suggests that Twelve Mile Creek is the main contributor of total As loading in Martindale Pond. The CHRC study did not report As concentrations. The PWGSC study reported that only sediments sampled near core site 2 had concentrations greater than the LEL.

SUMMARY

Organic contaminant loading, specifically TPH, above the SEL was found in areas directly related to the Welland Canal. The closest site to the Welland Canal, core site 39 (south end of Lake Gibson) had TPH values an order of magnitude greater than the O&G guideline limit. In addition, cores from the Old Welland Canal had TPH values that were greater than the O&G limit (Persaud *et al.*, 1992). Most sites tested along the Twelve Mile Creek from SHPP to the terminus near Martindale Pond did not have TPH concentrations greater than the O&G limit. Site 22 sediments sampled downstream of a storm sewer outfall at the end of Twelve Mile Creek, did have TPH values above the O&G limit. This is not surprising since the storm sewer services the QEW. All core sediments tested in Martindale Pond had TPH exceeding the O&G guideline.

The natural headwater tributaries of Twelve Mile Creek in SHPP (sites 34B and 34C) had sediments with total Ni, Cu, and Cr concentrations above the LEL. In addition, sediments from core 34C, representing a SHPP tributary of Twelve Mile Creek, contained elevated levels of As and Al (> LEL; see Figure 12). It was concluded that the same tributary contributed most of the Cd in sediments of core 34A (34A is located downstream of the junction of the tributaries; see Table 3). Metals in sediments sampled further downstream (south of Louth St.) in SHPP are a combination of these tributaries and an additional tributary upstream of site 33. Similar chemical characteristics were found in sediments between sites 33 and 34A with total Cu and Ni concentrations above the LEL and similar in magnitude, and with similar Pb, Zn, As, and Al concentrations. Total Cr and Cd sediment concentrations were much higher at site 33 than any other upstream cores (34A, 34B, 34C). All exchangeable metal fractions tested (34C) were below the lower limit (CCME, 1991) in SHPP.

Lake Gibson had two chemically distinct areas. This was observed in the TPH tests and in total and exchangeable metal contents. Core site 39, closest to the Welland Canal,

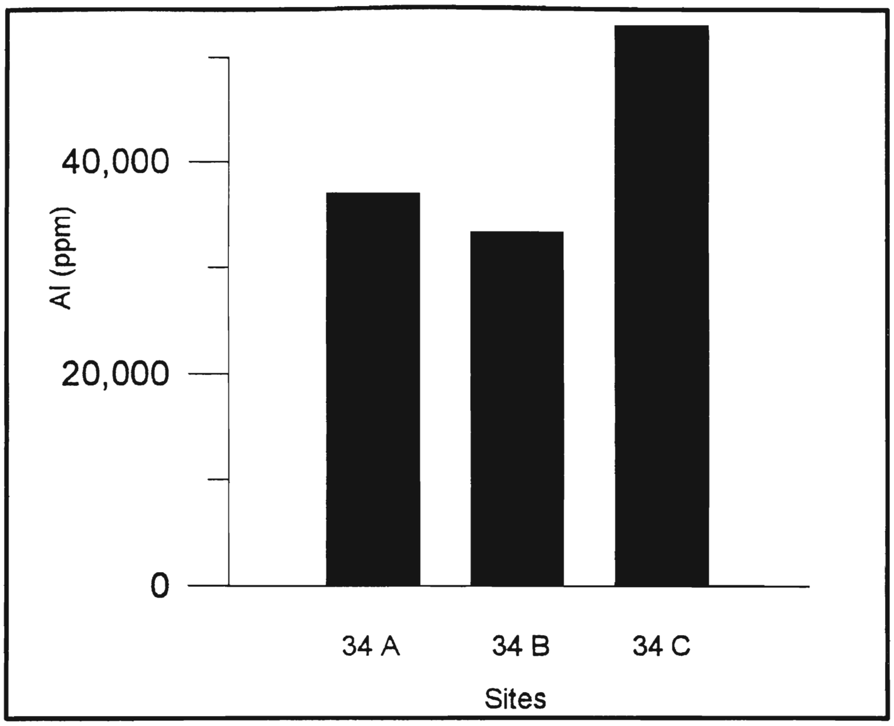


Figure 12: Average total Al concentration throughout depths for cores 34 A, 34 B, 34 C. Similar trends occur for Cr, and As (Short Hills Provincial Park).

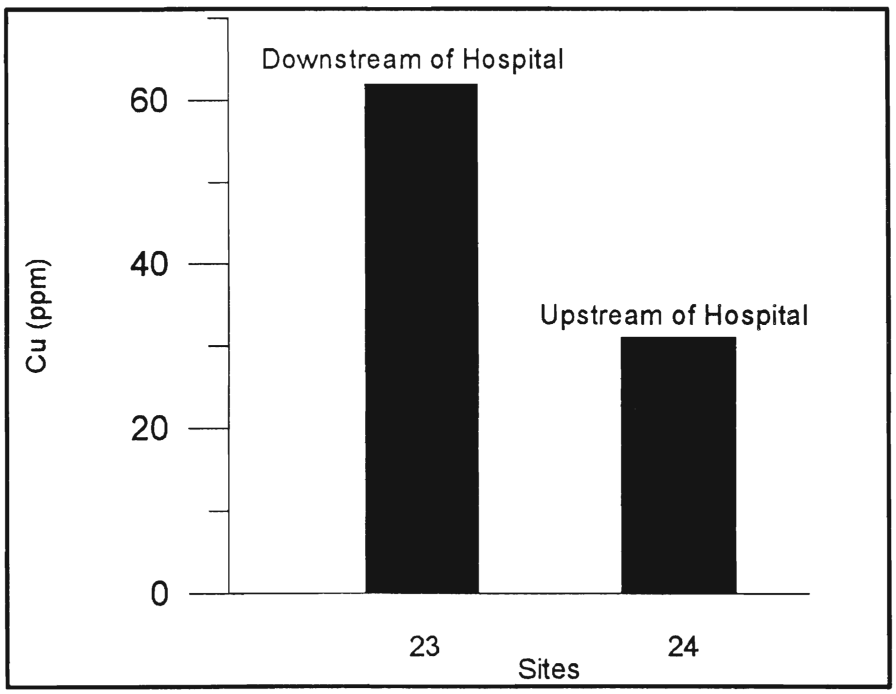


Figure 13: Total Cu concentrations throughout depths for cores (23 and 24) near the Hotel Dieu Hospital (reference point) along Twelve Mile Creek. Similar chemical trends were observed for total Al, Cd, Cr, Ni, Pb, and Zn.

probably represents a Welland Canal impact. All total metal fractions (Ni, Cd, Cu, Cr, Pb, As, Zn) tested in this area except Al were well above the SEL (usually by 2 orders of magnitude) and were the highest concentrations found in this study. The north area of Lake Gibson, in contrast, is representative of storm sewer outfall loading. Core sites 37 and 38 had sediments with total metals fractions (Ni, Cu, Cr, Pb, Zn, As, Al) greater than the LEL, except for Cd. Sediments from these cores also had exchangeable Pb greater than the upper limit. If the assumption that the north portion of Lake Gibson is more characteristic of the storm sewer input loadings than those derived from the Welland Canal, then there is a significant potential of anthropogenic impact.

Total and exchangeable metal contents fluctuated downstream of Decew Falls except in areas affected by storm, combined overflow, and industrial sewers. Site 30 downstream of Glendale Avenue and adjacent to a storm city outfall had total Ni, Cu, Cr, Pb, and Zn values similar to those of upstream sediments, with total Cd and As well above the LEL. Exchangeable metal fractions (Pb, Cr, Cu, Cd, and Al) were also elevated at site 30 and were above the upper limits (CCME, 1991). At site 25, where the Old Welland Canal empties into Twelve Mile Creek, all total metal levels (Ni, Cu, Cr, Cd, Pb, Zn, As, and Al) were greater than the LEL. In addition, total Ni, Cr, and As concentrations at some horizons were above the SEL. However, cores 25, 26, and 27 had total Cu values greater than the SEL. Exchangeable Pb and Cd were above the upper limits (CCME, 1991) in this area (site 26). In addition, the greatest exchangeable Cu concentrations in this study (>> upper limits) were found in sediments from the Old Welland Canal.

A city sewer outfall adjacent to the Hotel Dieu Hospital along Twelve Mile Creek is deemed the main contributor of increased total metal loading in sediments from site 23 (Ni, Cr, Cd, Al, Pb, Cu, and Zn; see Figure 13) relative to values sampled upstream from site 24. Total Cr in sediments from core 23 had concentrations greater than the SEL. Exchangeable metal concentrations also increased for Pb, Cu, Cd, and Al relative to values in sediments from site 24. Exchangeable Pb, Cu, and Cd sediment concentrations were greater than the upper limits (CCME, 1991) immediately downstream of the outfall (site 23). Exchangeable Cu doubled in magnitude below the outfall, relative to sediments sampled immediately upstream, while Al increased to levels above the upper limit.

Near the terminus of Twelve Mile Creek, below an area of numerous storm, combined overflow, and industrial outfalls are core sites C, and B. Further downstream, just upstream of Martindale Pond, are core sites 21, 22 and A. With the exception of Cr, the majority of the sediments representing this region have total metal contents (Ni, Cd, Cu, Al, Pb, As, and Zn) greater than the LEL. Areas closest to outfalls (C, A, and 22) have total Ni values greater than the SEL. Sediments from cores 21 and 22 have total As values greater than the SEL. This is most likely due to the storm sewer near site 22. Total Cd values were elevated at site 22 (Figure 14).

The majority of exchangeable metal fractions (Pb, Cr, Cu, Cd, Al, and Ni), from Twelve Mile Creek sediments just upstream of Martindale Pond, are above the upper limit. Elevated levels of Pb, Cu, Ni, and especially Cd were found at site 22. Figure 15 depicts a similar elevated exchangeable Cd trend as was seen in the total Cd values (Figure 14).

Site 21 was the only core of the entire study that can be interpreted as having a

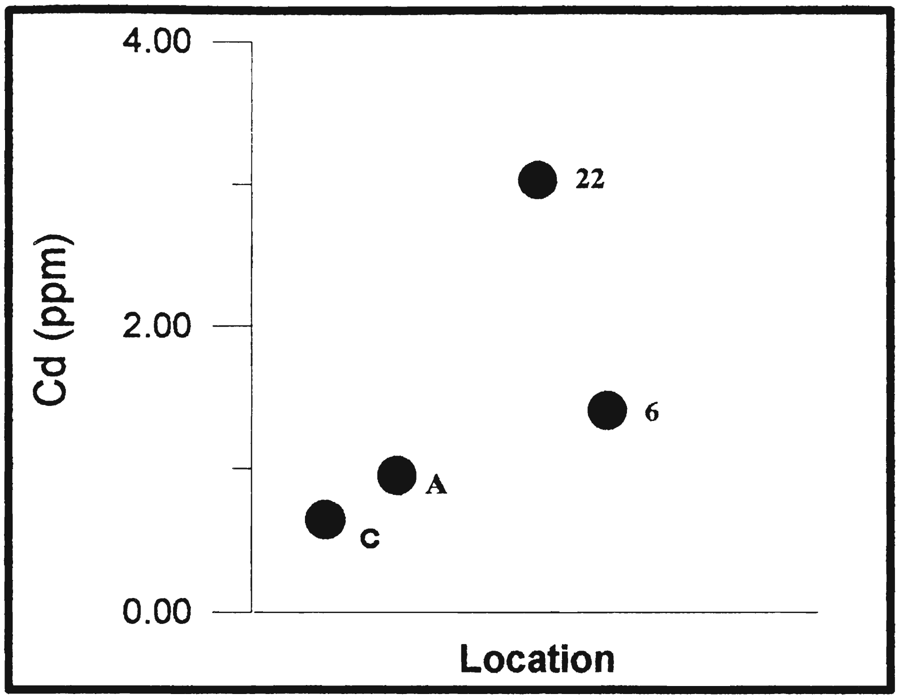


Figure 14: Total Cd averages throughout depths for selected cores in Twelve Mile Creek and Martindale Pond (see Figures 9 and 10). Note the high concentration in sediment from site 22.

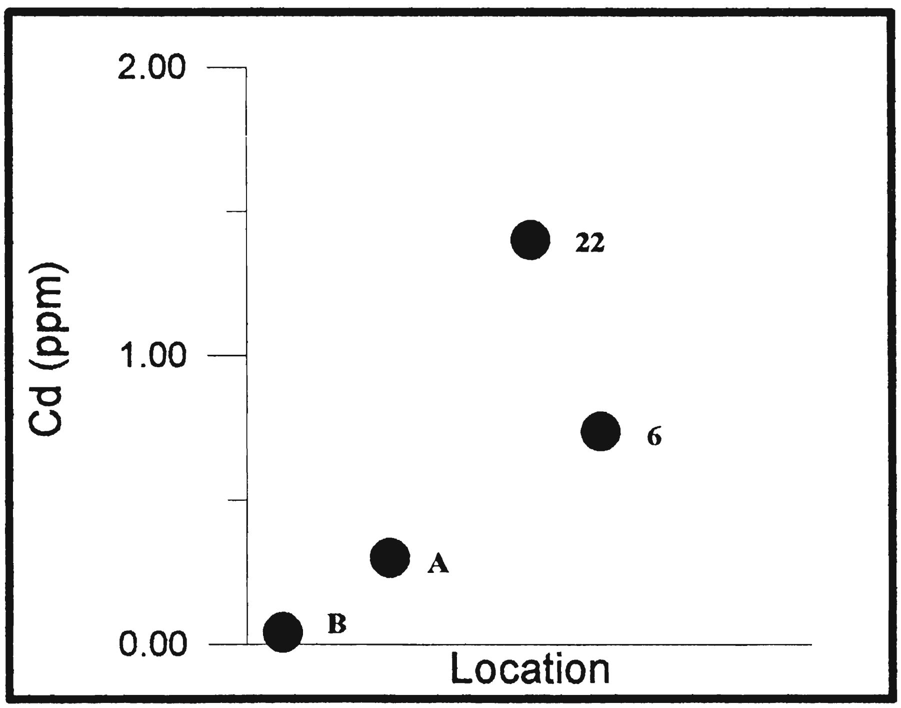


Figure 15: Available Cd averages throughout depths for selected cores in Twelve Mile Creek and Martindale Pond (see Figures 9 and 10). Note the high concentration in sediment from site 22.

classical metal distribution trend (Förstner and Wittman, 1983; see Figure 16). An increase in metal content towards the surface from depths 20.5 - 26 to 5 - 12 cm showing the migration of metals towards the surface of the oxidation/reduction zone and then is followed by a sharp cutoff in the oxidized layer.

Sediments from Martindale Pond have total metal (Ni, Cu, Cr, Cd, Pb, Zn, As, and Al) concentrations greater than the LEL. The elevated total Al concentrations in the north region near Michael Rennie Park and the south west region near Lookout Park, are most likely contributed by sediments derived from Richardson's Creek. Figure 17 depicts the distribution of total Al content in sediments from cores 4 and 6, of Martindale Pond, in relation to depth, representing metal input from Richardson's Creek and Twelve Mile Creek respectively. Total Ni values greater than the SEL were found at all sites in Martindale Pond except site O1 representing the north east portion of the pond. The north region, near Michael Rennie Park (site 2) had extremely high levels (>> SEL) of total Pb at depths below 72 cm. In addition, the north region and an area about the middle of the ponds contained total As levels well above the SEL. This is likely due to input of sediments derived from the Twelve Mile Creek. The majority of exchangeable metal fractions (Pb, Cu, Cd, Al, Ni) except Cr in sediments from the pond had concentrations above the upper limit.

In general, exchangeable Pb, Cu, Cd, Al, and Ni concentrations are more sensitive indicators of anthropogenic impacts than total metal values. For this reason, the MOEE should include in their guidelines categories for exchangeable metal fraction in sediments, because they more accurately represent potentially available toxic heavy metal contents.

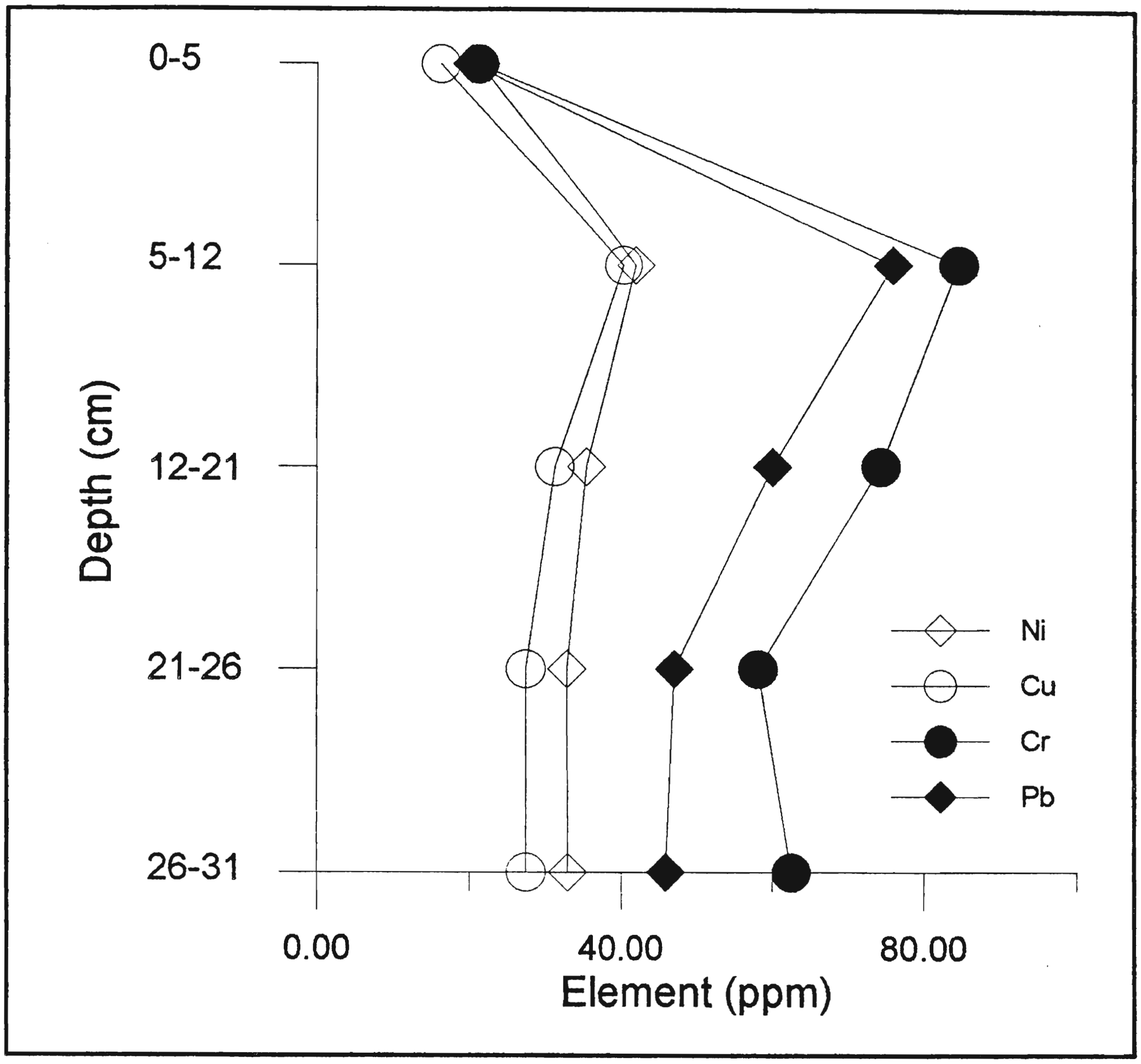


Figure 16: Total metal concentrations (Cr, Pb, Ni, Cu) in sediments from core 21 with depth depicting a classical total metal trend described by Förstner and Wittman (1983).

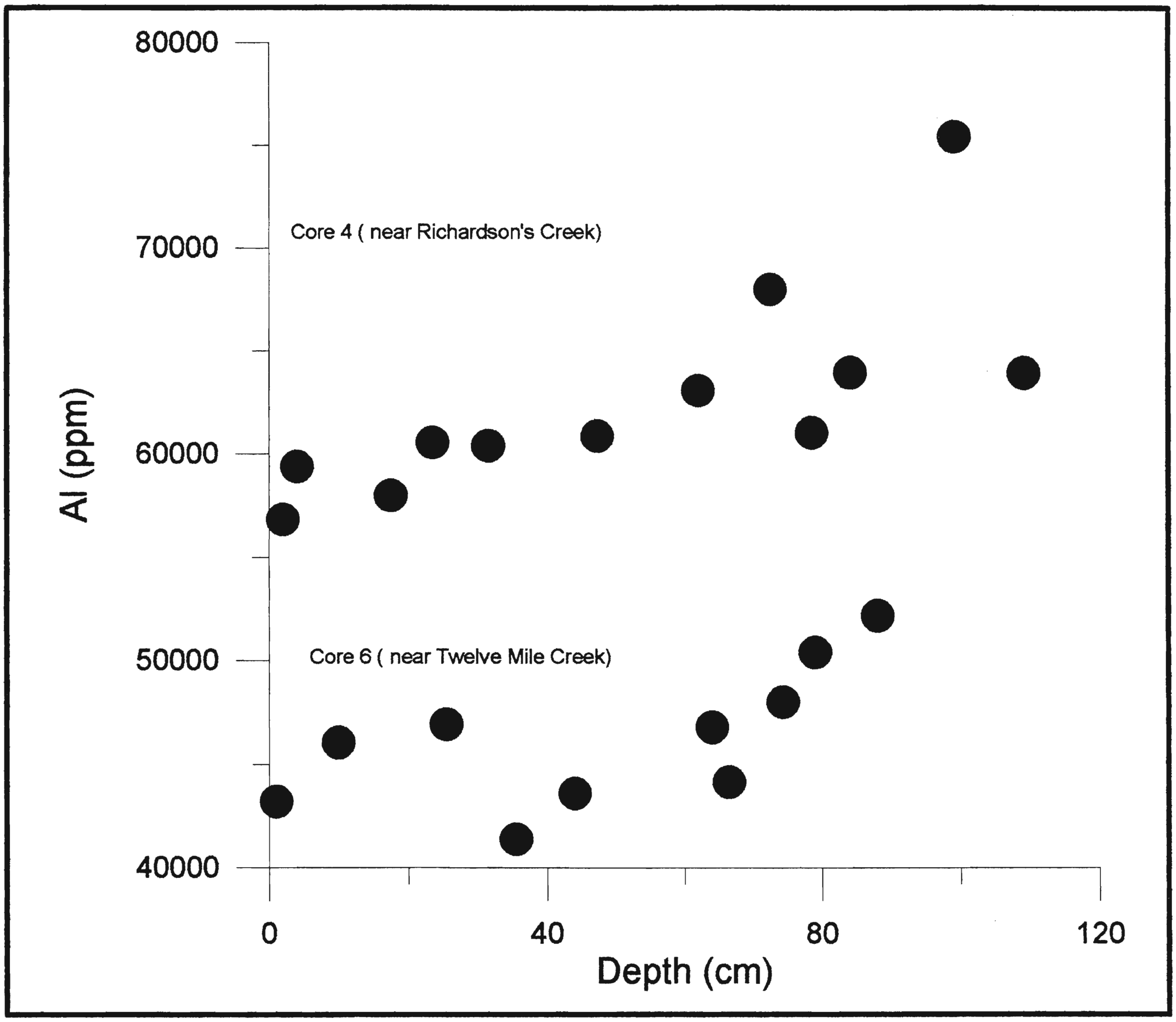


Figure 17: Total Al concentrations in cores 4 and 6 from Martindale Pond. Core 6 represents average concentrations in the majority of cores from Martindale Pond. Note core 4 sediments, derived from Richardsons Creek, have much higher Al concentrations.

CONCLUSIONS

The environmental assessment, based on total and exchangeable metal, and TPH content of sediments from the Twelve Mile Creek watershed leads to the following conclusions:

1. Total Pb and Zn and TPH contents in sediments from the headwater region (Short Hills Provincial Park) of the Twelve Mile Creek are well below their respective provincial guidelines.

2. In the following areas, some or several sediment horizons, exceed the metal (SEL) and Oil & Grease (O&G) MOEE guidelines:
   A. The south side of Lake Gibson (TPH, Ni, Cu, Cr, Cd, Pb, Zn, and As)
   B. Lower Old Welland Canal (TPH, Ni, Cu, Cr, and As)
   C. A segment of Twelve Mile Creek sediments downstream from General Motors Plant 4 (TPH, Ni, and elevated Cd (>>LEL))
   D. Twelve Mile Creek, upstream from the QEW (TPH, Ni, As, and elevated Cd (>>LEL))
   E. Martindale Pond: Sediments exceeded the TPH parameter, except near Michael Rennie Park, and total Ni values greater than the SEL. Total Pb and As fractions in sediments near Michael Rennie Park exceeded the SEL guideline. Total As exceeded the SEL in sediments from site 5 near the mouth of Martindale Pond.

3. Exchangeable metal fractions, using the CCME (1991) fresh water aquatic life limits are more sensitive in defining areas of environmental concern, with more values above guideline limits, than the total metal fraction guidelines of the MOEE. In addition, sediments with total Ni values greater than LEL (MOEE) had exchangeable fractions below the lower limit (CCME), thus identifying sediments with natural or tightly bound (possibly unavailable) metal contents.

CHAPTER 2

PASSIVE BIOMONITORING

ABSTRACT

A histochemical study of *Anodonta* sp., *Elliptio* sp. and zebra mussels (*Dreissena polymorpha*) was done in conjunction with passive biomonitoring of zebra and quagga mussels (*Dreissena bugensis*) from the Twelve Mile Creek watershed and Lake St. Clair (Jeanette's Creek, Chatham, Ontario). The highest concentrations of divalent metals such as Cu, Ni, Cd, and Zn, and trivalent Al appear to accumulate in gill and kidney tissues. Metal contents of organ tissues in *Anodonta* sp. vary with size class. Organ metal content varies among size classes, thus requiring consideration of size in biomonitoring studies. Shucked zebra and quagga mussel tissues, exhibited similar size class to Al content trends. In addition they reflected the Al content trends of top (approximately 10 cm) most sediments in the Twelve Mile Creek watershed. Quagga mussels appear to have higher Al concentrations than zebra mussels, thus suggesting that quagga mussels may be better passive biomonitors of Al. Zebra mussel tissues, Cd content, seemed to increase with size class trends. This was not demonstrated in quagga mussel tissues. This suggests that Cd may be regulated by quagga mussels and not by zebra mussels, and that zebra mussels may be better passive biomonitors of Cd than are quagga mussels.

INTRODUCTION

Environmental standards tend to focus on biogeochemical analyses of general compartments such as air, water and sediment when setting risk and remediation limits for particular ecosystems. Water quality criteria devised for drinking, irrigation and general water uses based on the analysis of water are unsatisfactory because it gives little information on the amounts of a chemical entering directly or indirectly by diffusion an organism and its tissues (Raymont, 1972; Price and Skei, 1975). Equally unsatisfactory is the setting of water quality criteria based on water sampling programs. Instead, a multiple sampling scheme is needed to eliminate natural variation in metal concentration with time, season, freshwater run-off, overturning, and other physicochemical/hydrological factors (Gross, 1971, 1972; Phillips, 1977). The limitations of setting water quality criteria based on water samples becomes clear when the exact nature of the detrimental impact of chemical species are considered in the ecological health of aquatic biota.

Biological monitors or indicators may consist of the entire organism (soft and/or hard tissue), a part of it, or a single tissue compartment. Total body burden chemistry may not be representative of toxicological endpoints such as growth-life termination or temporary-permanent interruption of the reproduction process. A biological monitor should fulfill the following parameters and characteristics (Butler *et al.*, 1971; Haug *et al.*, 1974; Phillips, 1977):

1. the organism should accumulate the pollutant without being killed by the levels encountered,

2. the organism should be sedentary in order to be representative of the area of collection,
3. the organism should be abundant in the study area,
4. the organism should be sufficiently long-lived to allow the sampling of more than one year-class,
5. the organism should be of reasonable size, giving adequate tissue for analysis,
6. the organism should be easy to sample and hardy enough to survive in the laboratory, allowing defecation before analysis and laboratory studies of the uptake of chemicals.
7. the organism should exhibit a high concentration factor for chemicals allowing direct analysis without pre-concentration,
8. a simple correlation should exist between the chemical content of the organism and the average chemical concentration in the surrounding water,
9. most importantly, all organisms in a survey should exhibit the same correlation between their chemical content and those in the ambient water, at all locations studied under all conditions.

Thus, it is imperative that environmental water variables, such as salinity, pH and temperature, are known or standardized before population comparisons are attempted. In addition to these hydrological variables, other interfering effects, such as season, growth rate, weight, size, and sampling position of the organism, have to be considered in any valid biomonitoring study. In addition, biological elemental fractionation (Bryan, 1986; Brand, 1994) between the aqueous medium and the organism, at any level of chemical content may not necessarily reflect ambient water conditions but simply an organism's regulatory process.

Bivalves have been studied extensively for their biomonitoring capabilities. They tend to concentrate chemicals in their soft tissue and to a lesser degree in their hard parts (shell; Anderson, 1977; Brand *et al.*, 1987; Rollins *et al.*, 1987; Herwig *et al.*, 1989). Thus, chemical analyses are relatively straightforward and do not require specialized treatments (Phillips, 1977). These organisms are filter-feeders and obtain their chemical composition from their food, the solution, and from the ingestion of inorganic particulate material (Moore, 1971). It has been suggested by a number of laboratory studies that food may be the major contributing factor in chemical uptake by mussels (Pentreath, 1973; Schulz-Baldes, 1974; Preston, 1971; Boyden and Romeril, 1974). Similarly, numerous studies on organism weight, size, age or sex have found that these variables need to be considered in any study using mussels as biomonitors of pollution. Metal concentrations are particularly susceptible to seasonal influence of the environment on body burden composition (e.g., Pentreath, 1973; Bryan, 1973; Fowler and Oregioni, 1976). The co-presence of several metals in the same ambient environment as to their indifferent, antagonistic or synergistic effect has to be elucidated before a chemical may be a considered an indicator of contamination (Phillips, 1977).

The ability of bivalves to concentrate toxic chemicals in their soft tissue and hard parts makes them environmentally hazardous to human consumption but excellent biomonitors of local pollution (Anderson, 1977; Fischer *et al.*, 1993; Brand *et al.*, 1987; Rollins *et al.*, 1987; Herwig *et al.*, 1989). Analytical results of chemicals in the body tissue are usually expressed on either a dry or wet weight basis. Tissue preparation prior to analysis and body burden calculation becomes a major consideration in obtaining consistently representative chemical content values for environmental comparisons (Simpson, 1979; Mersch and Pihan, 1993).

In most studies of mussels as biomonitors of pollution, the total soft tissue of an organism was generally shucked and total soft tissue residue was examined for chemical loading (e.g., Amiard *et al.*, 1987; Kraak *et al.*, 1992; Kraak and Lavy 1993; Mersch and Pihan, 1993; Fisher *et al.*, 1993; Richman, 1994). Histochemical analyses of specific tissues are relatively rare. When histochemical analyses were done, they tended to concentrate on just one metal (specifically Cd; e.g., Bias and Karbe, 1985; Herwig *et al.*, 1989; Hemelraad and Herwig, 1988; Holwerda *et al.*, 1988; Hemelraad *et al.*, 1990). Even fewer studies considered more than one metal accumulating to steady state within various tissue compartments (Karbe *et al.*, 1975; Anderson, 1977; Hemelraad *et al.*, 1990; de Kock and Bowmer, 1993). Overall, these studies demonstrated sublethal effects and that steady state conditions in zebra mussels are reached after about 40 to 60 days. Small mussels usually equilibrate within 21 days, whereas larger freshwater mussel take longer than 21 days to achieve equilibrium with the ambient water (Hemelraad and Herwig, 1988; de Kock *et al.*, 1993; Mersch and Pihan, 1993).

Any study, using organisms as biomonitors of pollution must at all times be aware of reproductive cycles (gonad development or loss) and regulatory processes (phosphate salt granule formation) which change the whole tissue weight and metal content (Borcherding, 1991; Hemelraad and Holwedra, 1990; Mersch and Pihan, 1993). Additional stress, such as toxic metal detection, can produce acidosis behaviour (Borseth *et al.*, 1995), thus altering normal biological activities. Field and laboratory studies, through observations, must identify and account for these types of monitoring stresses.

For the second part of the study several bivalves, *Dreissena polymorpha* (zebra mussel), *Anodonta* sp., and *Elliptio* sp., were dissected and histochemically analysed, so that comparisons between different organisms and their organ metal contents could be made. In addition, *Dreissena polymorpha* (zebra mussel), and *Dreissena bugensis* (quagga mussel) from Twelve Mile Creek watershed and Lake St. Clair (Jeanette's Creek) were examined to compare the anthropogenic impact on the two watersheds. The shucked soft tissues were analysed for their metal contents and, where possible, size classes were compared. In addition, zebra and quagga mussels were compared when multiple size classes were used. It is hoped that the combination of a sediment quality database, gathered in Chapter 1, in conjunction with aquatic invertebrate data will provide a better understanding of the environmental health of the Twelve Mile Creek watershed.

METHODS

Sampling

Dreissena polymorpha (zebra mussel) and *Dreissena bugensis* (quagga mussel) were sampled at three different localities, sites 10 (15 m radius sweep in front of storm sewer S14, Figure 2) and 16 (approximately 30 m north east of core site 2, along the retaining wall of Michael Rennie Park, Figure 10) in Martindale Pond and between sites 37 and 38 (Figure 4) in Lake Gibson, of the Twelve Mile Creek watershed. Sampling in Twelve Mile Creek was hampered by safety precautions, since zebra mussels were observed only at times of low flow (controlled by Ontario Hydro at the Decew Falls) in the deeper parts of the creek bed where colonization is possible. Mussels were collected in Port Colborne Harbour (North East section) within a 50 m radius of the shore line, and zebra mussels were also obtained from

Jeanette's Creek (Lake St. Clair). No suitably large zebra mussels were found at Johnston Harbour (Tobermory). Instead, freshwater clams were sampled within a 50 m by 4 by 3 m snorkel sweep. The unionids will be used as reference material and active biomonitors, and were identified as *Anodonta* sp. and *Elliptio* sp. using Clarke (1981).

Experimental

Due to differences in tissue digestion techniques used by various workers (Simpson, 1979; Hemelraad et al., 1990; Mersch and Pihan, 1993; Houston pers. comm., 1994), an experiment was devised to establish consistent parameters, to prevent machine degradation by use of highly acidic samples, while obtaining acceptable results. In addition to the mussels and clams collected from the various water-bodies, some blue mussels, *Mytilus edilus,* were purchased from a grocery store in Hamilton, Ontario for comparison purposes. The mussels were shucked from their shells, and all tissues were oven dried (65 °C). Dried tissue was homogenised by powdering. A duplicate sample was made for each sample. Tests were conducted to determine 1, the length of time required for digestion, 2, the concentration of HNO_3 (Analytical grade, quartz distilled) and 3, the various processes of agitation/digestion (shaking at room temperature or still digestion at elevated temperatures). Times of acid digestion ranged from 4 to 72 hours. Acid concentrations ranged from 0.25 to 10% (v/v). Samples were allowed to cool, centrifuged at 3000 rpm for 15 to 20 minutes, filtered and brought up to mark in 10 mL volumetric flasks. Filtrate was analyzed for three metals (Pb, Zn, Cd) using normal flame AAS technique.

Test Results. The 72 hours of acid leaching test gave the best reproducible results (Appendix 2). Figure 18 shows oven and shaker values for the different acid concentrations.

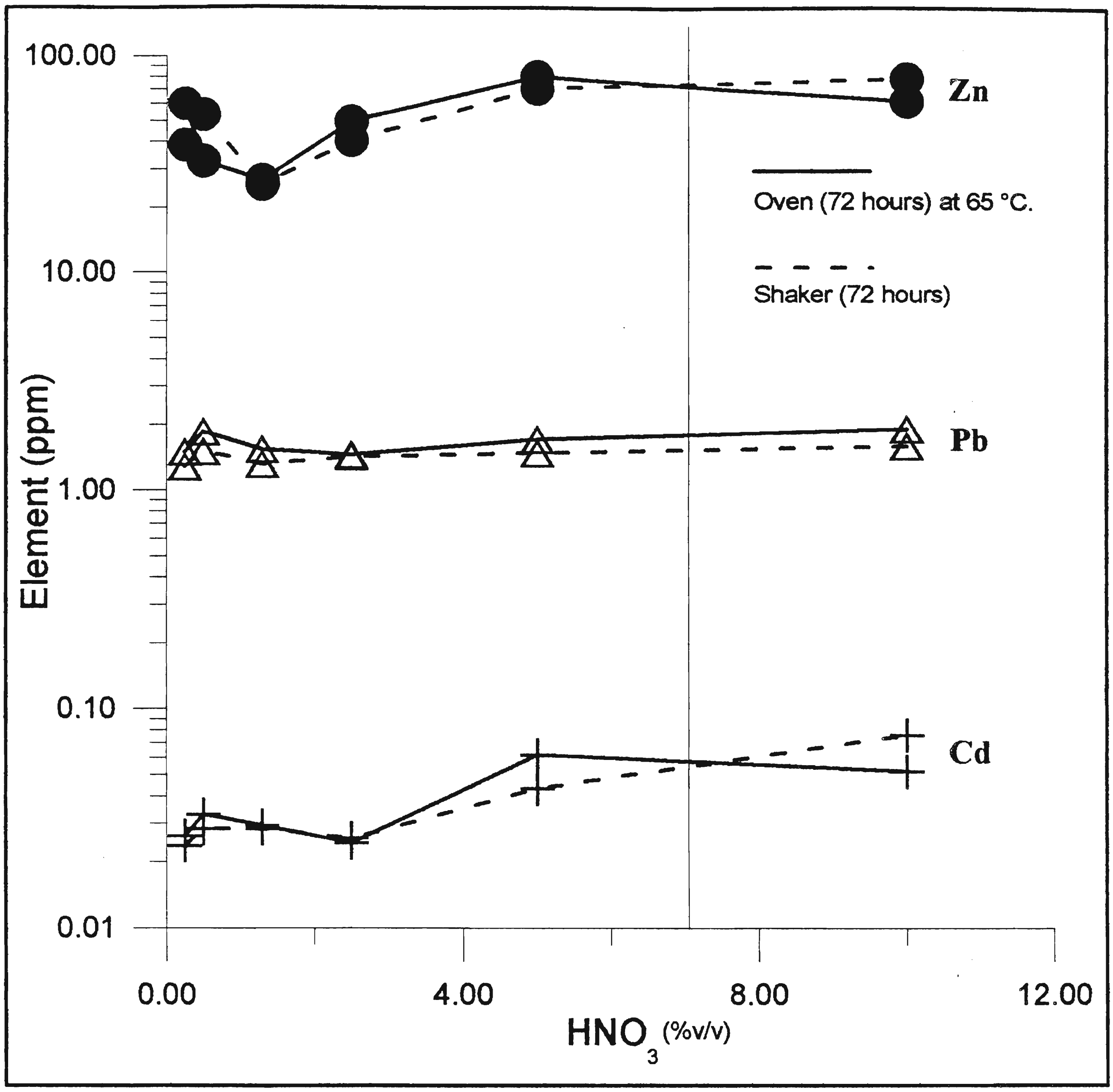


Figure 18: Relationship between oven heated (72 hours at 65 °C), shaker agititated (72 hours) and percent acid for digested *Mytilus edilus*.

Note: Test runs for 4 and 24 hours are significantly lower and can be found in Appendix 2.

Linear approximations were not possible, but it was determined that an acid strength of 7% (v/v) HNO_3 produced the most consistent metal concentration results. At concentrations between 5.0 and 10.0% (v/v), the oven-heated acids produced more concentrated samples. Fluctuations could be explained by the natural variation in samples, because whole animals were shucked and homogenisation was difficult. The results were used to devise the method described below.

Samples were placed in beakers and oven-dried for 3 weeks at 65 °C to facilitate total drying. Samples were then homogenized by powdering using a mortar and pestle or by cutting into fine pieces using dissecting scissors. Samples of approximately 0.25 g, weighed to four decimal places, were used. After addition of 10 mL of 7% (v/v) HNO_3, to each sample, they were placed into the oven for 72 hours. An oven-aided digestion time of 72 hours was found to give the most consistent chemical results. Afterwards, samples were allowed to cool and centrifuged at 3000 rpm to remove any solutions retained within cellular walls. Samples were filtered, using medium porosity ashless filter paper, into 10 mL flasks. Samples were brought up to mark using distilled and quadruply-deionized water, poured into tests tubes, capped and stored at 4 °C until analysis.

Biomonitor Dissection and Preparation

Animals were kept in the laboratory under continuously flowing tap water for 4 to 5 days to facilitate cleaning of the gut. The organisms were then identified as 'classic' zebra or quagga mussels using the shape parameters discussed by Pathy and Mackie (1993). Organisms that would require scanning electron microscopy for identification were not used. Each of the species was then measured for total length, with calipers, and separated into size classes ranging from 1.5 to 3.5 cm, in 0.5 cm increments, and > 3.5 cm. Size classes must have at least 12 or more organisms, (Kraak *et al.*, 1992; Mersch and Pihan, 1993). In this study, in each area of biomonitoring, 20 to 30 individuals were pooled to obtain a representative sample.

Mussels were dissected with stainless steel instruments, such as curved and straight jeweller forceps, as well as straight and curved micro scalpels. All zebra and quagga mussels were dissected by making an initial incision between the valves anterior to posterior byssal retractor muscle and posterior to the umbo. This is possible because in this region there is a wide enough gap between the valves to fit a scalpel. A downward cut followed by an upward cut through the muscle tissue adjacent to the shell, was used to kill the mussel so that the valve could be separated. The bysuss was removed to minimize contamination. Zebra and quagga mussels were then shucked into glass beakers.

One particular experiment (**Histochemical Location**) required total dissection of zebra mussels. This was performed by the removal of the organism from the shell, by carefully scraping the muscle tissue away from the shells, while minimizing puncturing of the mantle. The organism was then removed and placed into a petri dish of deionized water under a microscope for dissection. It was imperative to minimize organs damage, in particular the pericardial sac, so the heart could could be identified by the pulsating action. The various organs were identified, sampled, and placed into glass beakers.

Zebra mussels collected from site 10 (Martindale Pond) were sorted into a size class of 2.7 to 3.2 cm length. The mussels were allowed to actively filter in tank (lab) water for

3 weeks, and thus are not representative of site 10 metal content. Thirty specimens were pooled after dissecting and shucking the remains, and analyzed as discussed above. Targeted organs included the gills, gut, foot and bysuss, muscle (anterior adductor and posterior adductor), kidney and residual tissues. Contamination by the bysuss is possible because of incorporation (trapping) of substrate material. Caution must therefore be used in interpreting foot/bysuss results. The small size of the kidney contributed to experimental error because the pooled dry kidney did not meet the minimum weight criteria. In addition its location made it difficult to separate it from the other organs. The kidney compartment usually included the proximal limb, distal limb, and the kidney itself, and portions of the heart and rectum (Morton, 1993). An attempt was made to sample mostly kidney material with minor muscle tissue. However, cross contamination probably did occur by incorporating some gut (stomach) material. The category 'residual' describes all material that was not sampled previously. This includes gonads, digestive gland, and mantle tissue.

Unionids sampled from Johnston Harbour, Tobermory were separated into several size classes, (*Anodonta* sp., 100, 109.5, 119, and 136 mm average length; *Elliptio* sp., 98.5 mm average length; ranges can be found in Appendix 2) for histochemical analyses and size class comparison. Similar to zebra and quagga mussels, *Anodonta* sp. could be easily opened by one incision on the dorsal side between the valves. The scalpel was then run along the shell to the posterior region where it was possible to sever the adductor muscle allowing for insertion of a tool to pry open the valves. *Elliptio* sp. has larger adductor muscles which required two separate incisions. In addition to the incision previously mentioned, another cut was made along the ventral side towards the umbo to cut the anterior adductor muscle. The valves were separated with a stainless steel spatula to expose the muscle groups and to allow for dissection. Once opened the shells were tipped and the fluid decanted. Dissections were performed inside the shells. The mantle tissue was carefully cut and treated as a sample (Freeman and Bracegirdle, 1971; Pearse and Pearse, 1987). The pericardial sac, connective intestine and rectum were removed and named heart and rectum. The gills (both inner and outer) were sampled and treated as one. Occasionally the gills were filled with gonads and glochida, but whenever possible the gills were treated as a separate sample. The foot was identified and cut according to the extent of the continuous texture and colour region, where the upper foot (visceral mass with intestine and gonads) was identified as the region below the dark membrane (kidney) immediately ventral to the heart and rectum and above the foot. The stomach, digestive gland, and midgut collectively named gut were identified as the darker organs connected to the upper foot, and were sampled in conjunction with the upper foot. All muscle tissue was collected and sampled as one. Due to the small size of the kidney, the removal was intricate, and only in some instances was the kidney removed without cross-contamination from other organs such as the gills, gut and/or gonads. All samples were placed into glass beakers and treated as previously described.

Tissue Analysis

Tissues were analyzed for eight to twelve elements using various AAS and GFAAS techniques. Ni, Cu, Al, Cr, Zn, and Cd were analyzed as previously discussed (see **Total Metal Analysis**, Chapter 1). Be, As, Mo, Co, Se, and Pb were analyzed by graphite furnace. Percent error was calculated using duplicates (Chapter 1, Table 1).

RESULTS

Histochemical Location

Zebra Mussels. The relative chemical concentrations in the various organs (Histochemical location) of zebra mussels are presented in Figure 19. Concentrations in mussels are organ specific and provide the best case that metal toxicity may indeed be influenced by local lethal doses. The highest concentration of Cu appear to be in the gills, with slightly lower levels in the gut/kidney combination. The lowest Cu levels (< 0.10 ppm) appear to be observed in the foot-bysuss material (Figure 19).

Nickel levels are seem to be highest in the foot/bysuss material, with similar Ni contents of the 20 - 25 ppm range in the gill samples. The other three tissue groups exhibit Ni values of approximately 10 ppm (residual, muscle-kidney, gut-kidney; Figure 19).

Similar to the high Ni content in the foot-bysuss, Pb content is highest in this compartment (Figure 19). The Pb content is higher in the foot-bysuss by a factor of 4 than in other mussel organs.

Cd content is relatively low in all organ compartments tested (Figure 19). The highest and lowest levels appear to be in the gut-kidney and residual sample groups, respectively.

Zn concentrations were highest in the muscle-kidney group (Figure 19). Since the kidney weight fraction of this compartment is small, it is assumed that most of the Zn is contributed by the muscle tissue. The other four compartments exhibit similar levels of Zn,

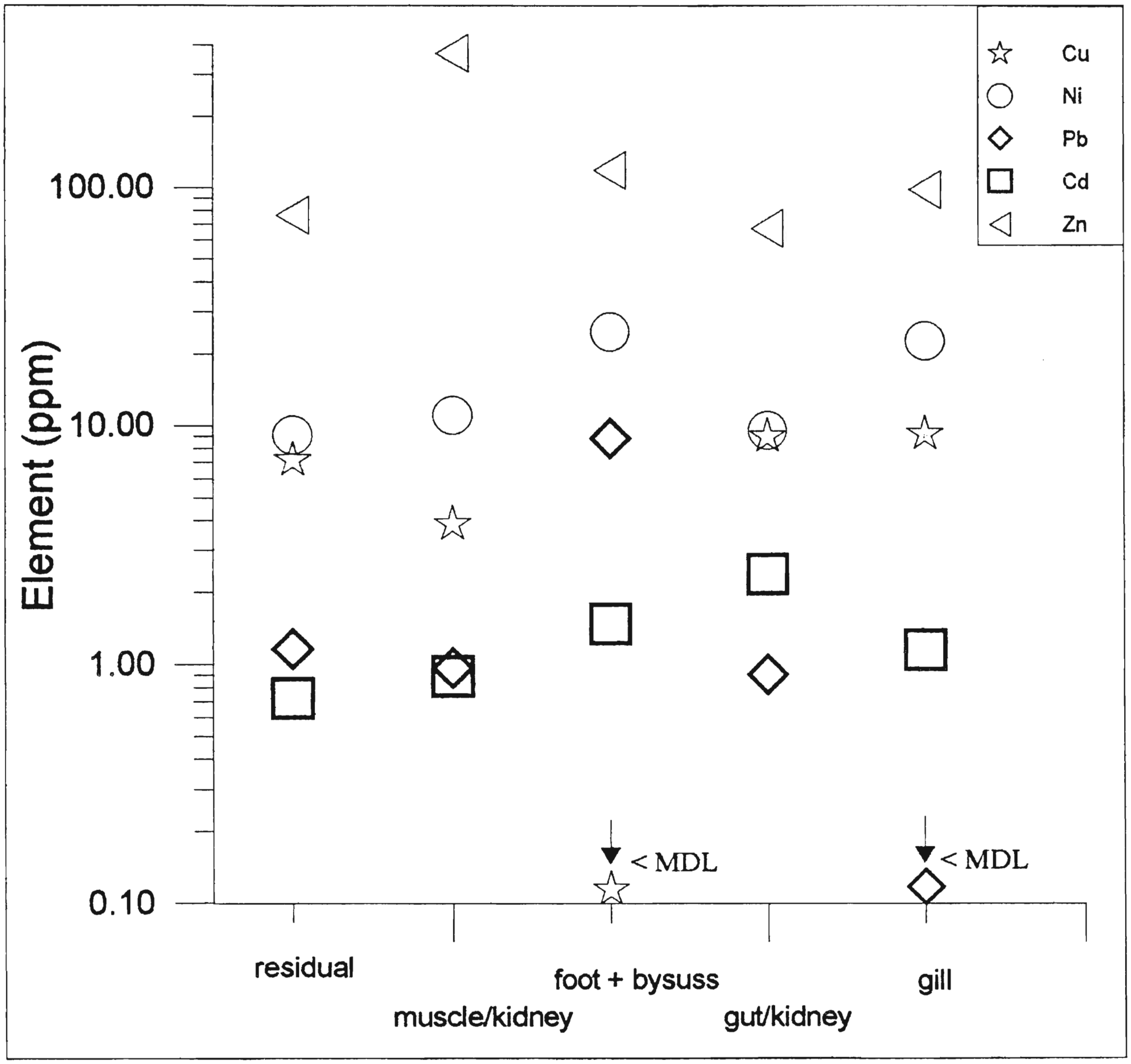


Figure 19: Histochemical location of metals in various organs of zebra mussels from Martindale Pond (site 10). Data are limited to 2.7-3.2 cm size class. Note: residual contains digestive gland, gonads, and mantle tissue.

which are lower by about a factor of four compared to that found in the muscle-kidney fraction.

Fresh Water Clams. Some of the unionids from Johnston Harbour were used as reference mussels. The following discussion deals mainly with results obtained from testing *Anodonta* sp. organs. Because of the paucity of *Elliptio* sp. material, their metal concentrations are listed in Appendix 2, and only highest organ values are mentioned in the discussion section.

Overall there appears to be a decrease in the cumulative Cu content in the organ groups with increasing specimen size. The overall Cu content decreases from about 100 ppm in the 100 mm size group to about 40 ppm in the 136 mm one (Figure 20). Considering individual organs, all except the mantle which was not sampled in the 119 mm size class, show a small decrease in Cu content of with size. In contrast, the greatest apparent change was observed in the Cu content of the gills which decreased from 50 ppm in the 100 mm size class to 8 ppm in the largest size class (Figure 20). Other compartments (kidney, mantle, foot, and gut) also seemed to decrease in Cu content with size, but at a smaller rate of change. Highest Cu concentrations were found in the 100 and 109.5 mm size class gills and in the 119 mm size class kidney tissues.

Total Ni content (gut, kidney, and gill) appears to decrease with increasing size for the first three size classes (17 to 4 ppm), which is followed by a sharp increase in the 136 mm (33 ppm) size class (Figure 21). Gut and kidney organs seemed to decrease in Ni content from the 100 to 119 mm size group. In contrast, gill tissue Ni content appears to decrease in

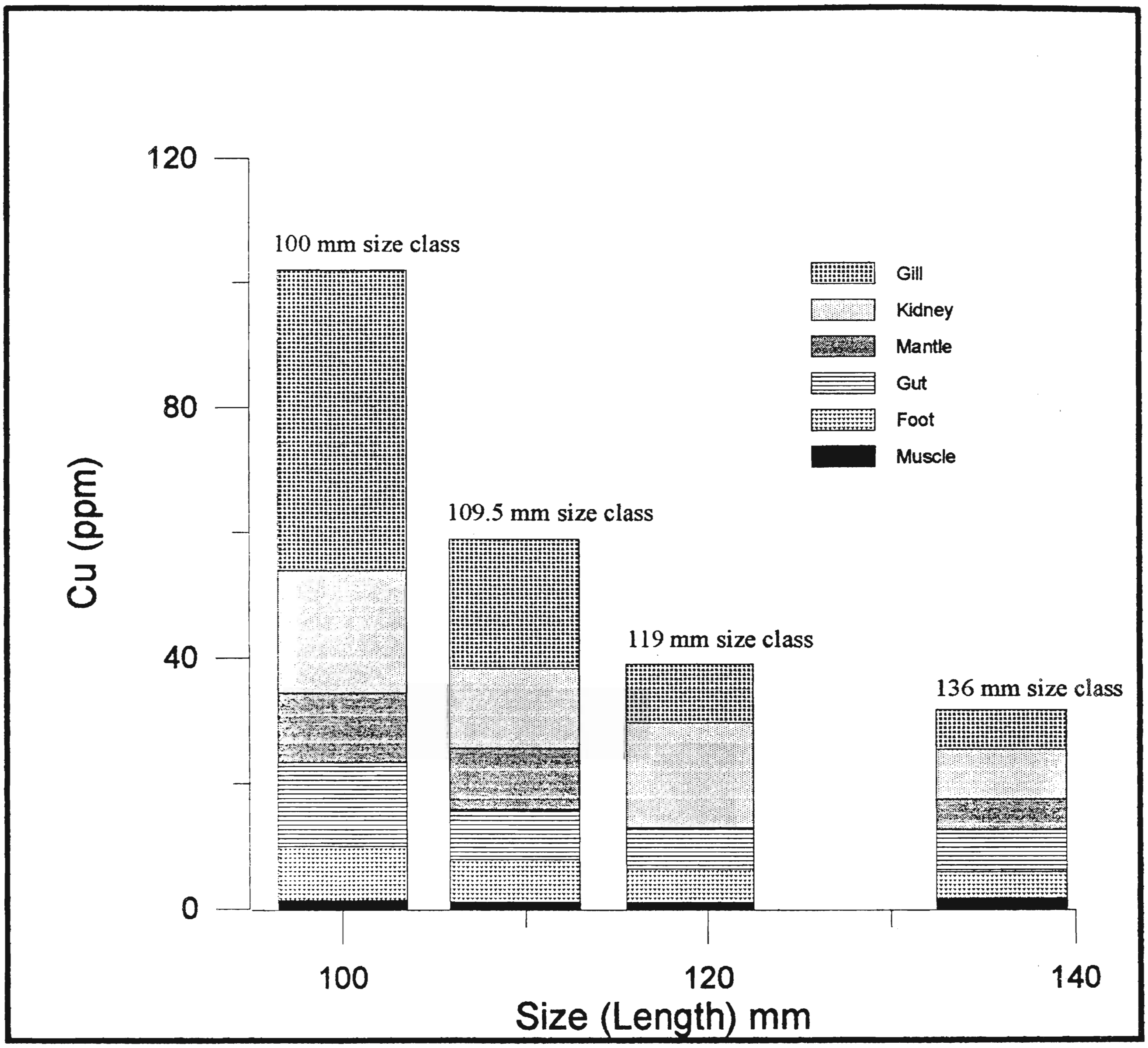


Figure 20: **Relationship between Cu (dry weight) and shell length in *Anodonta sp.* in selected organ groups.**
Note: Mantle tissue for the 119 mm size class was not sampled.

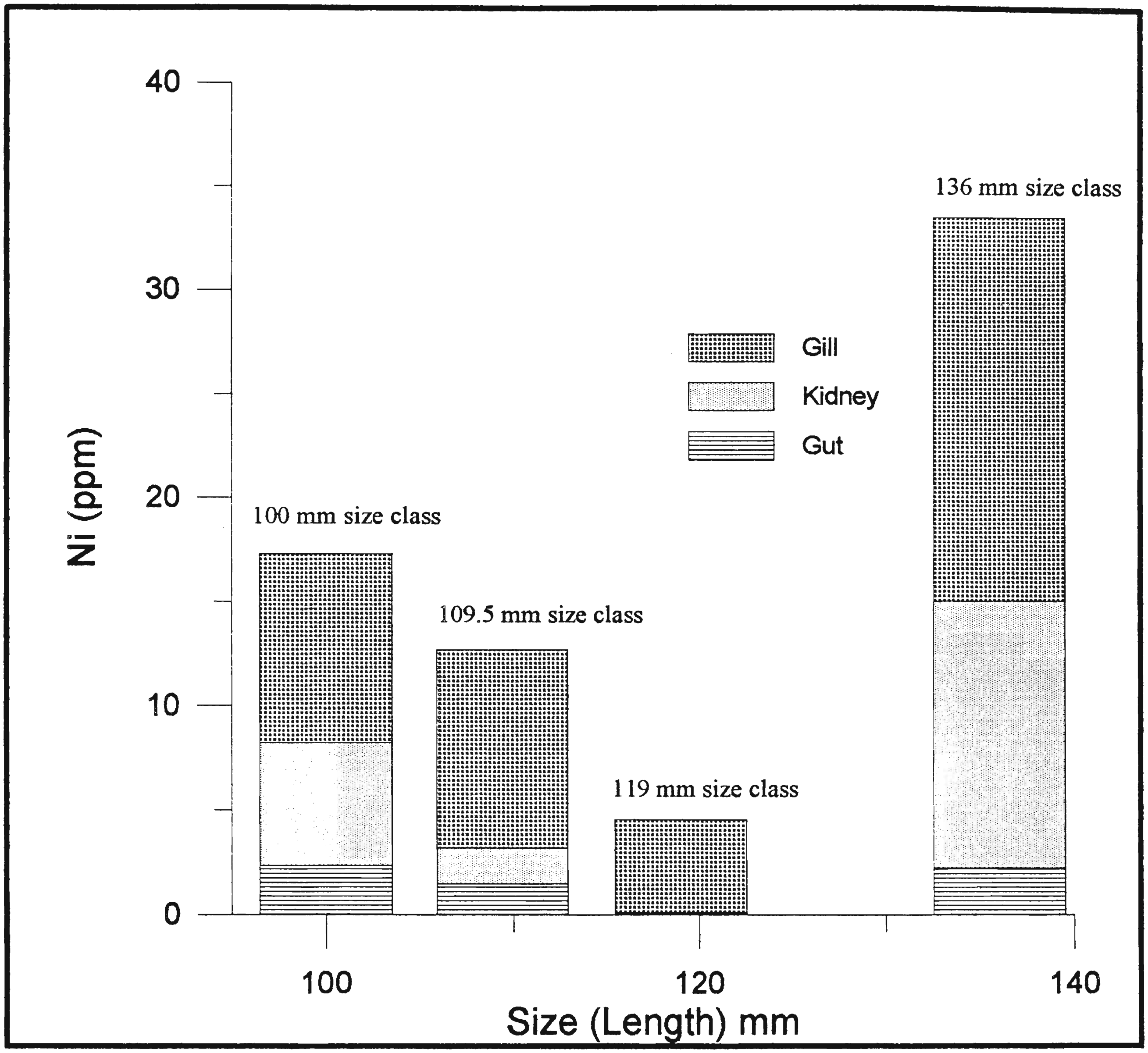


Figure 21: **Relationship between Ni (dry weight) and shell length in *Anodonta sp.* in selected organ groups.**
Note: Mantle tissue for the 119 mm size class was not sampled.

the first three size classes and increase in the 136 mm size class. The gill tissues appear to consistently have the highest Ni concentrations over the entire size class range.

Total Zn concentrations are similar with around 1400 ppm in the first three size classes (Figure 22). Apparent decreases in Zn content, from 1350 to 1050 ppm was observed from the 119 to 136 mm size classes. The kidney, foot, and gut Zn concentrations had similar trends with increasing size. Specifically, the Zn content seems to decrease from the 100 to 109.5 mm size group, increase from the 109.5 to 119 mm size group, and decrease again in the largest size group. In contrast, the mantle Zn content had opposite trends appearing to increase with specimen size. Mantle Zn contents seemed to increase from the 100 to 119 mm size group and decrease in the 136 mm size group. Similarly, muscle tissue Zn contents seemed to increase in the first three size classes and slightly decreased in the 136 mm size class. The foot Zn concentrations seemed to be similar, with about 120 ppm in all size classes. The highest Zn concentrations were noted in the gill and kidney for each of the size classes.

Overall the Cd content appears to decrease from the 100 to 119 mm size class and increase in the largest size class (Figure 23). Individually, the heart and rectum, gill, mantle, and kidney groups Cd concentrations seems to decrease from the 100 to 119 mm size class and the gill, mantle and kidney tissues increase in Cd content in the largest size class, whereas the heart and rectum Cd content seems to decrease below the detection limit. The gut, foot, and muscle organ groups Cd concentrations appears to have decrease from the 100 to 109.5 mm size class, increase in the next larger size class, and decrease in the largest size class. The kidney tissues have the highest Cd concentrations.

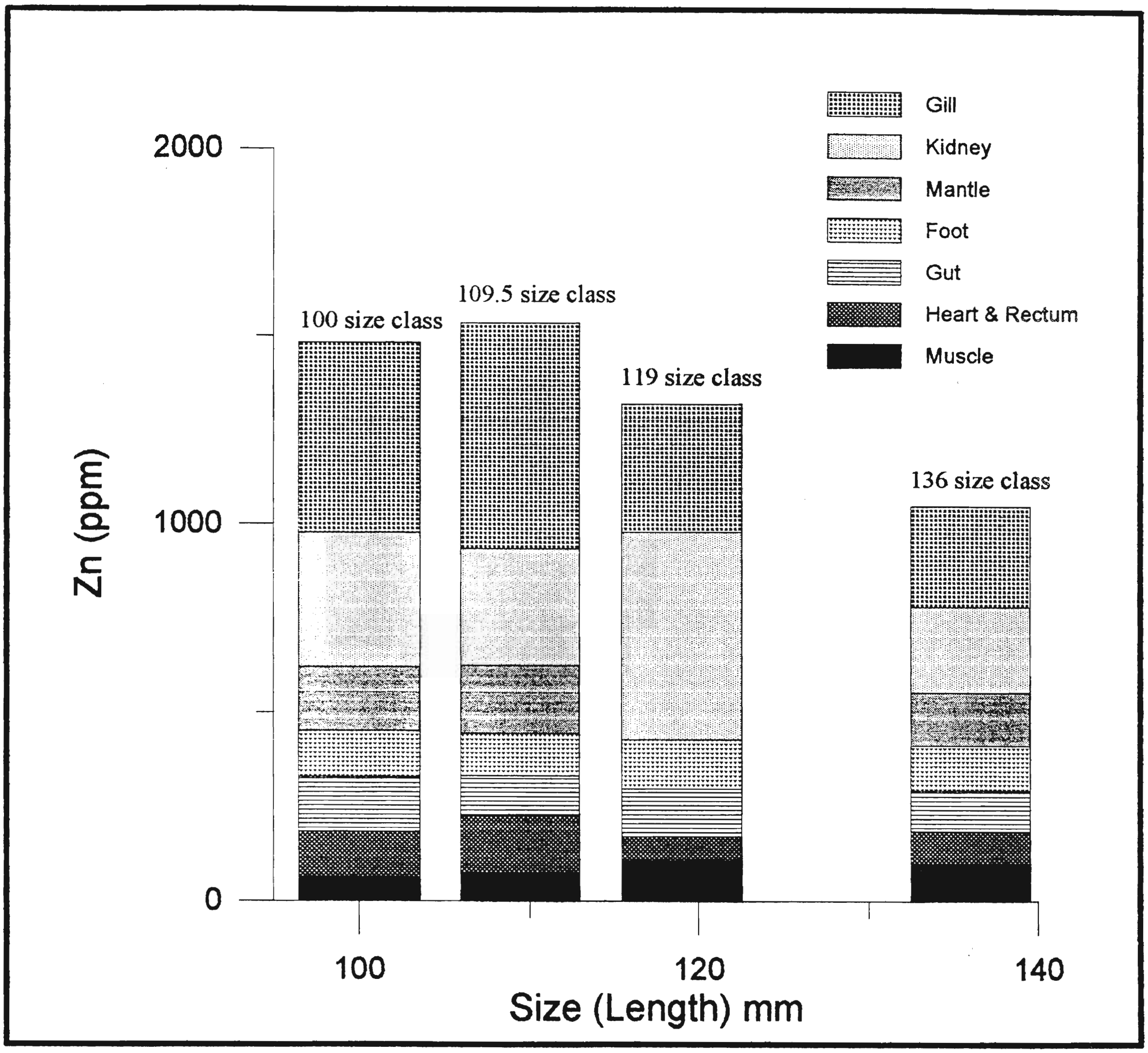


Figure 22: **Relationship between Zn (dry weight) and shell length in *Anodonta sp.* in selected organ groups.**
Note: Mantle tissue for the 119 mm size class was not sampled.

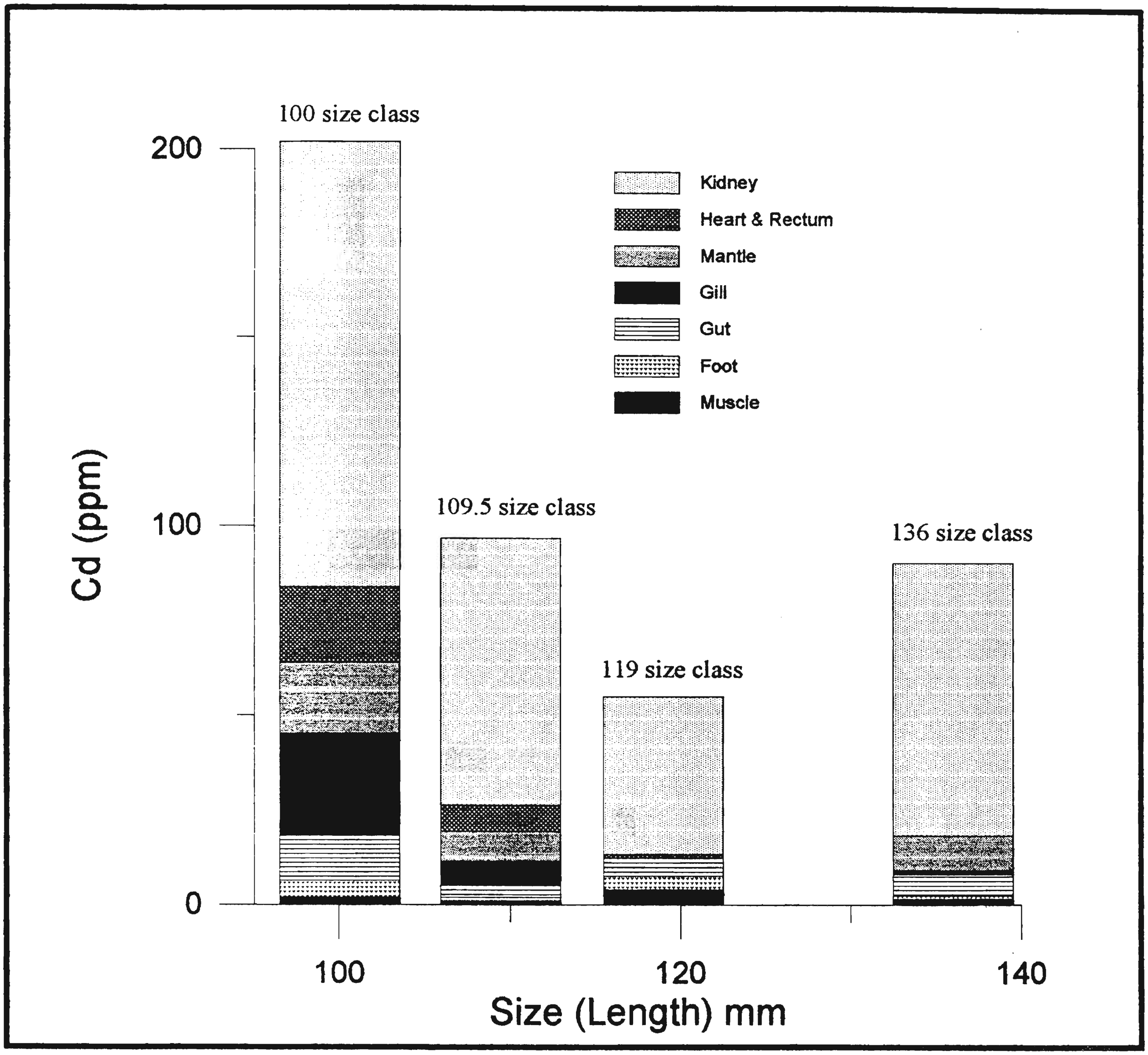


Figure 23: **Relationship between Cd (dry weight) and shell length in *Anodonta sp.* in selected organ groups.**
Note: Mantle tissue for the 119 mm size class was not sampled.

The cumulative kidney, muscle, mantle, gut, gill, and foot cumulative Al concentrations appear to increase from the 100 to 119 mm size class, and are followed by a sharp decrease in the 136 mm size group (Figure 24). All organs, except heart and rectum (not plotted) and gills seem to increase in Al concentrations in the first three size classes, whereas the gill Al content seems to decrease from the 100 to 109.5 mm size class and increase in the 119 mm size class. Mantle tissue Al contents appear to increase in the 136 mm size class, while the other organ groups Al content appear to decrease. The greatest Al concentrations were found in the gill, mantle, kidney, and mantle tissues for size classes, 100, 109.5, 119, and 136 mm, respectively.

Overall, cumulative Pb contents appear to decrease with increasing size and increase in the 136 mm size class (Figure 25). Individually, except for the mantle tissue, Pb content seems to fluctuate with increasing class size, and consistent trends were not observed between the organ groups. The mantle tissue Pb contents appear to increase slowly and steadily with increasing size. The highest Pb concentrations were found in the 100 mm heart and rectum, and 109.5 mm size gill tissues and in the 119 and 136 mm size heart and rectum tissues.

Passive Biomonitoring Survey

Twelve Mile Creek Watershed. Only one size class of zebra and quagga mussels obtained from Port Colborne Harbour, was evaluated in this survey. This limits comparisons of chemical trends between size classes. One size class of quagga and two of zebra mussels were obtained from Martindale Pond (site 10). In contrast, site 16 (Martindale Pond) and Lake Gibson specimens ranged from 1.75 to 3.25 cm (zebra mussel) and 1.75 to 2.75 cm (quagga mussel) and separated into four and three size classes, respectively. Their shucked

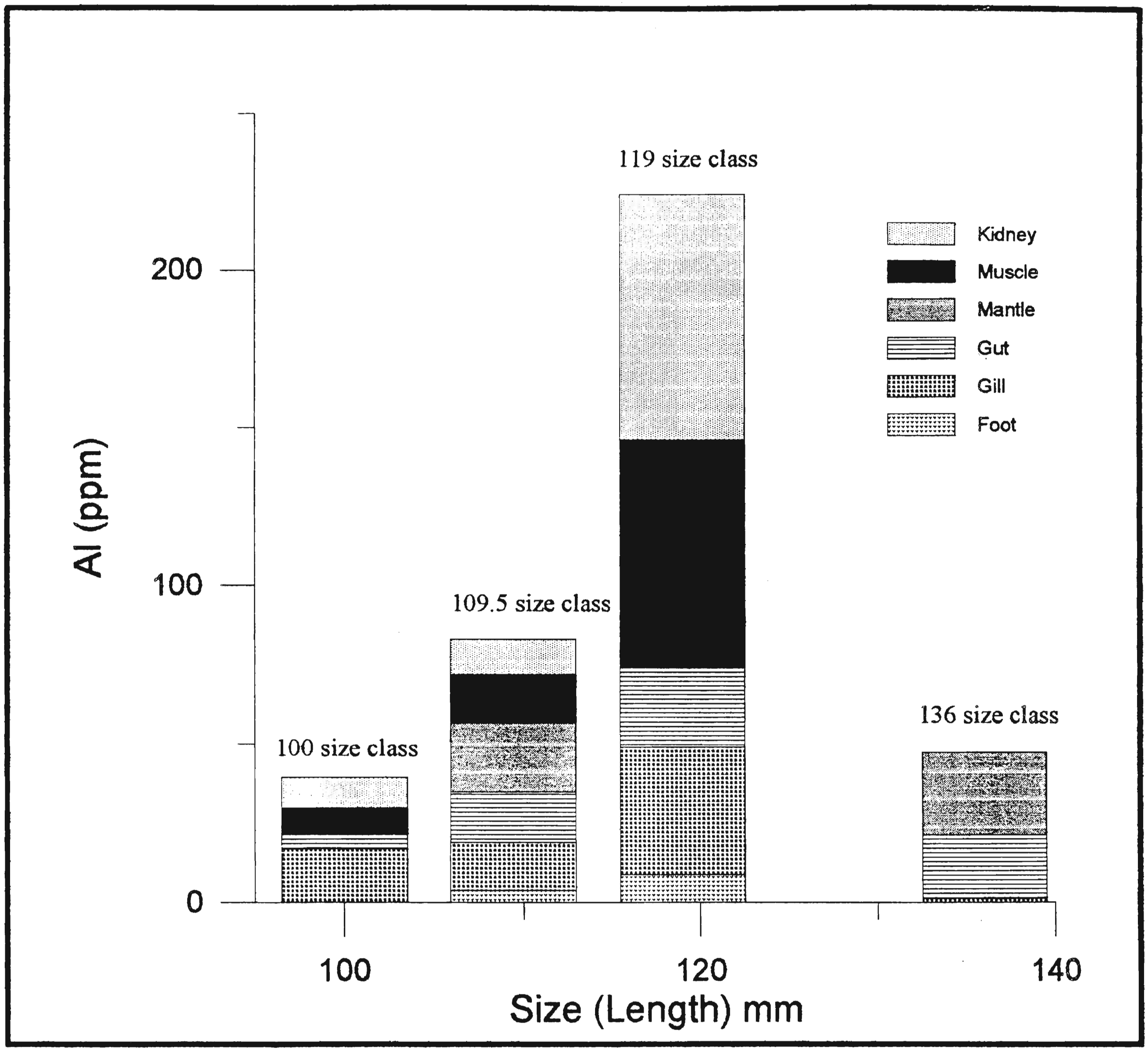


Figure 24: **Relationship between Al (dry weight) and shell length in *Anodonta sp.* in selected organ groups.**
Note: Mantle tissue for the 119 mm size class was not sampled.

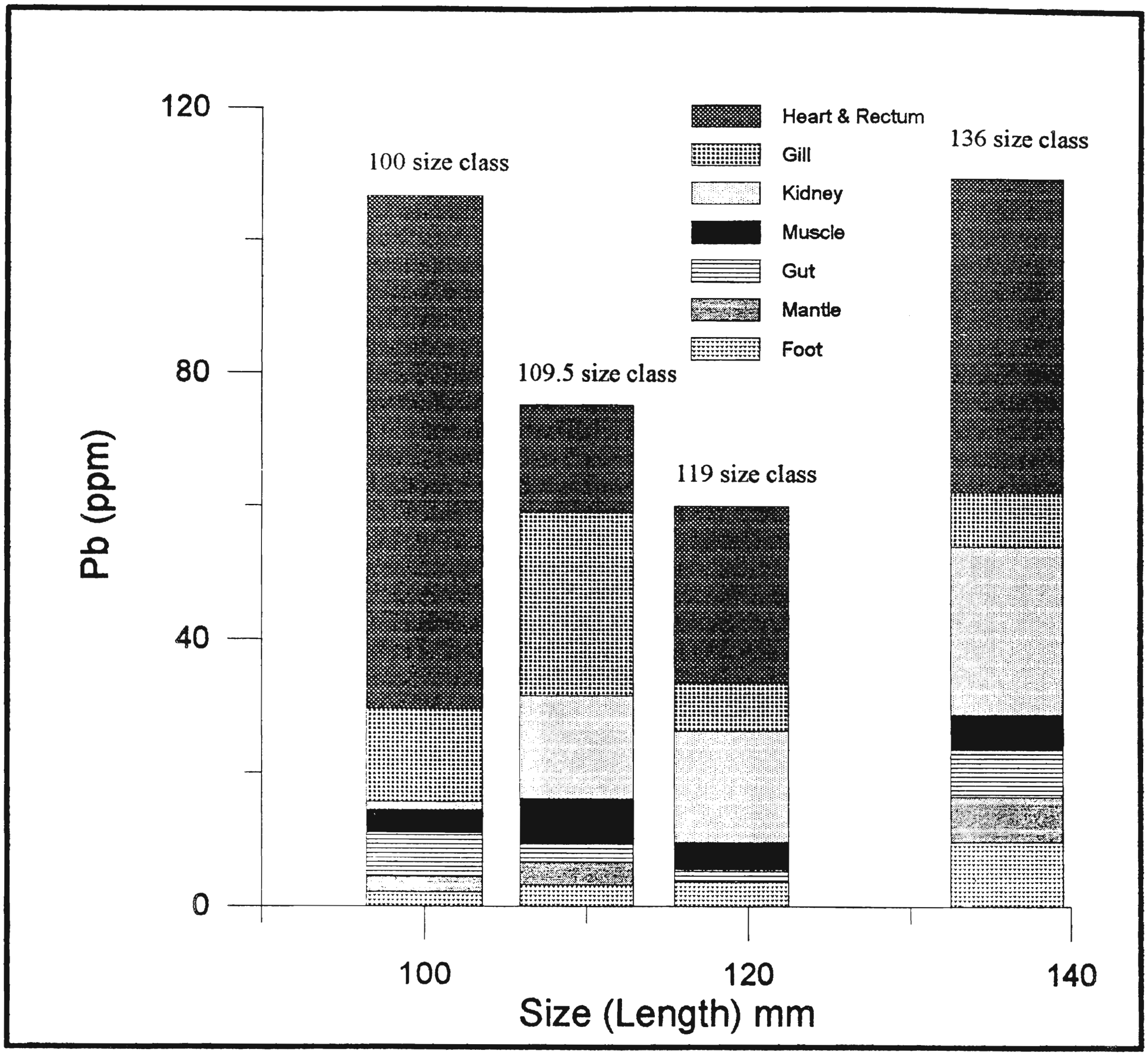


Figure 25: **Relationship between Pb (dry weight) and shell length in *Anodonta sp.* in selected organ groups.**
Note: Mantle tissue for the 119 mm size class was not sampled.

mussel dry-weight concentrations are plotted against average class size in Figures 26 - 32.

Zebra and quagga mussel tissues from Port Colborne Harbour appear similar with about 13 - 15 ppm Cu despite the difference in size (Figure 26). In contrast, the 2.75 cm size class for zebra and quagga mussels from site 10 (Martindale Pond) seem to have similar amounts of Cu, whereas the 3.25 cm zebra mussel size class contains almost twice as much Cu as the smaller size class. The Cu content of the specimens from site 16 (Martindale Pond) and Lake Gibson (especially) appear higher than those from the other localities. The site 16 zebra mussels seem to exhibit a decreasing Cu trend with increasing size class. Similarly site 16 quagga mussels appear to have a faster decreasing Cu trend with increasing size class (Figure 26). A possibly similar trend and rate in Cu content with size class was also observed in the zebra and quagga mussels from Lake Gibson (Figure 4).

Zebra mussel tissues appear to have higher Ni contents than quagga mussels of the same size class. The 2.75 cm size class of quagga mussels from site 10 (Martindale Pond) seems to contain the smallest amount of Ni (Figure 27). Site 10 and 16 zebra and quagga mussels show a small increase in Ni with increase in size class, whereas the Ni content of the zebra mussels from site 10 appears to double from the smaller (2.75 cm) to the larger (3.25 cm) size class. The Lake Gibson specimens seem to exhibit increasing Ni trends with increasing size class in both the zebra and quagga mussels, with a greater rate of Ni increase in zebra mussel tissue.

Zebra mussels Zn content of the 2.75 cm size class appears to be greater in Port Colborne specimens than for site 10 specimens (Martindale Pond), with highest amount of

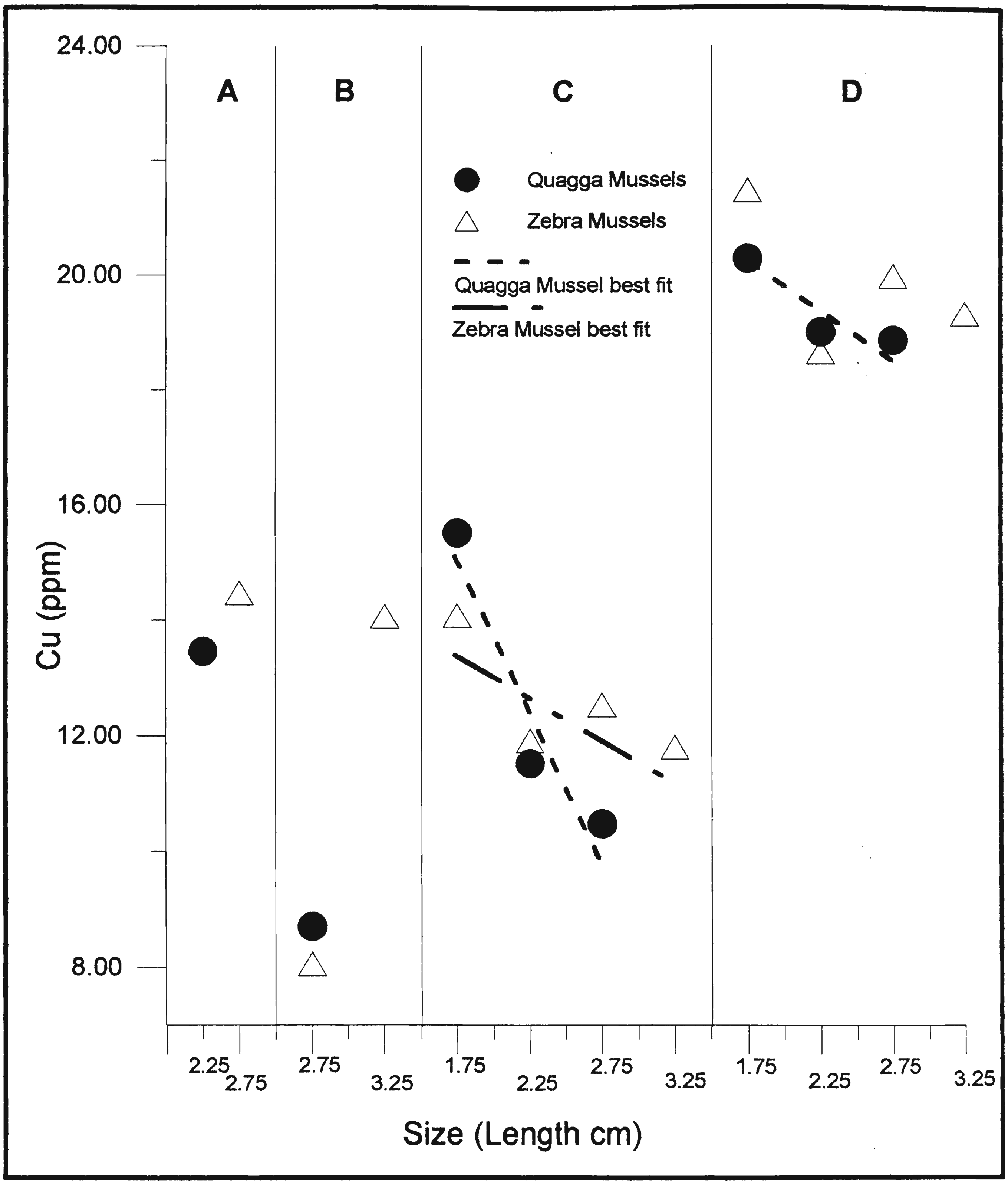


Figure 26: Relationship between Cu (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

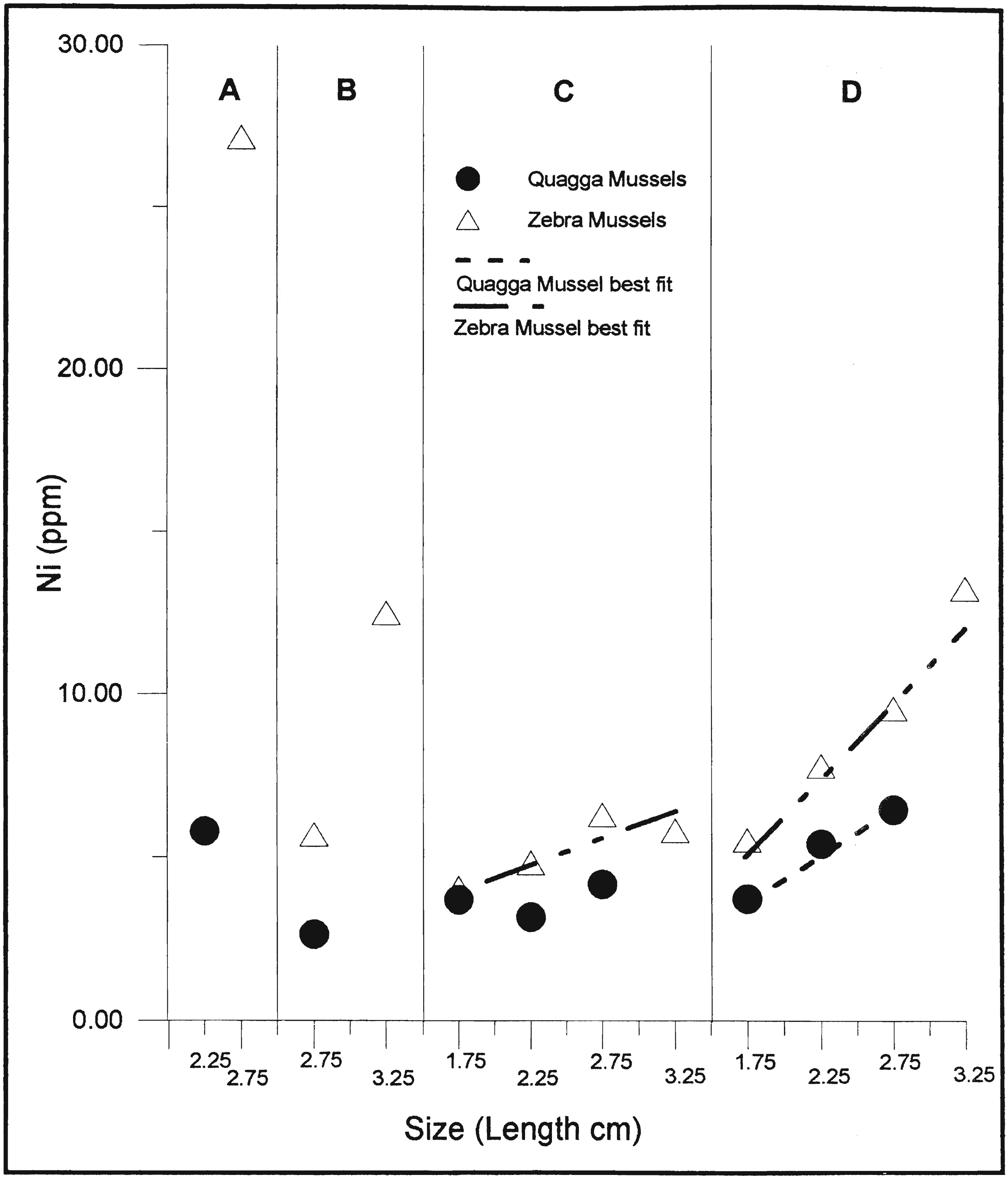


Figure 27: Relationship between Ni (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

Zn in the 3.25 cm size class (Figure 28). Zinc contents of specimens from site 16 (Martindale Pond) seem to be lower than those from the other localities. Site 16 zebra mussels appear to have an increasing Zn trend with increasing size class, whereas the quagga mussels appear to have a rapidly decreasing Zn trend with size class. In contrast, apparent increasing trends in Zn content with size class were observed in the zebra and quagga mussels from Lake Gibson, with a greater rate of change in the quagga mussels with size.

Quagga mussel tissues appear to be greater in Al content than zebra mussel tissues (Figure 29). The 2.25 cm Port Colborne quagga mussels are a size class smaller than the zebra mussels (2.75 cm size class) and yet both seem to contain similar amounts of Al. In contrast, the Al content of site 10 (Martindale Pond) zebra mussels appears lower and seems to decrease with increasing size class. Apparent decreasing and increasing Al trends with size class were observed in the specimens from site 16 (Martindale Pond) and Lake Gibson, respectively. This applies to both zebra and quagga mussels. Quagga mussels seem to have greater rates of Al uptake than zebra mussels.

Most zebra and quagga mussel tissues sampled, appear similar with less than 2 ppm Cd despite the differences in size class (Figure 30). In contrast, the 3.25 cm size class, zebra mussels from site 10 (Martindale Pond), contains 14 ppm of Cd. This is may be an error, however a similar trend was observed for Pb in the same tissue sample. Site 16 (Martindale Pond) and Lake Gibson zebra mussels seem to have increasing Cd trends with increasing size class. The site 16 quagga mussels appear to exhibit decreasing Cd trend with size class, whereas the Lake Gibson quagga mussels do not appear to increase or decrease in Cd content with size class.

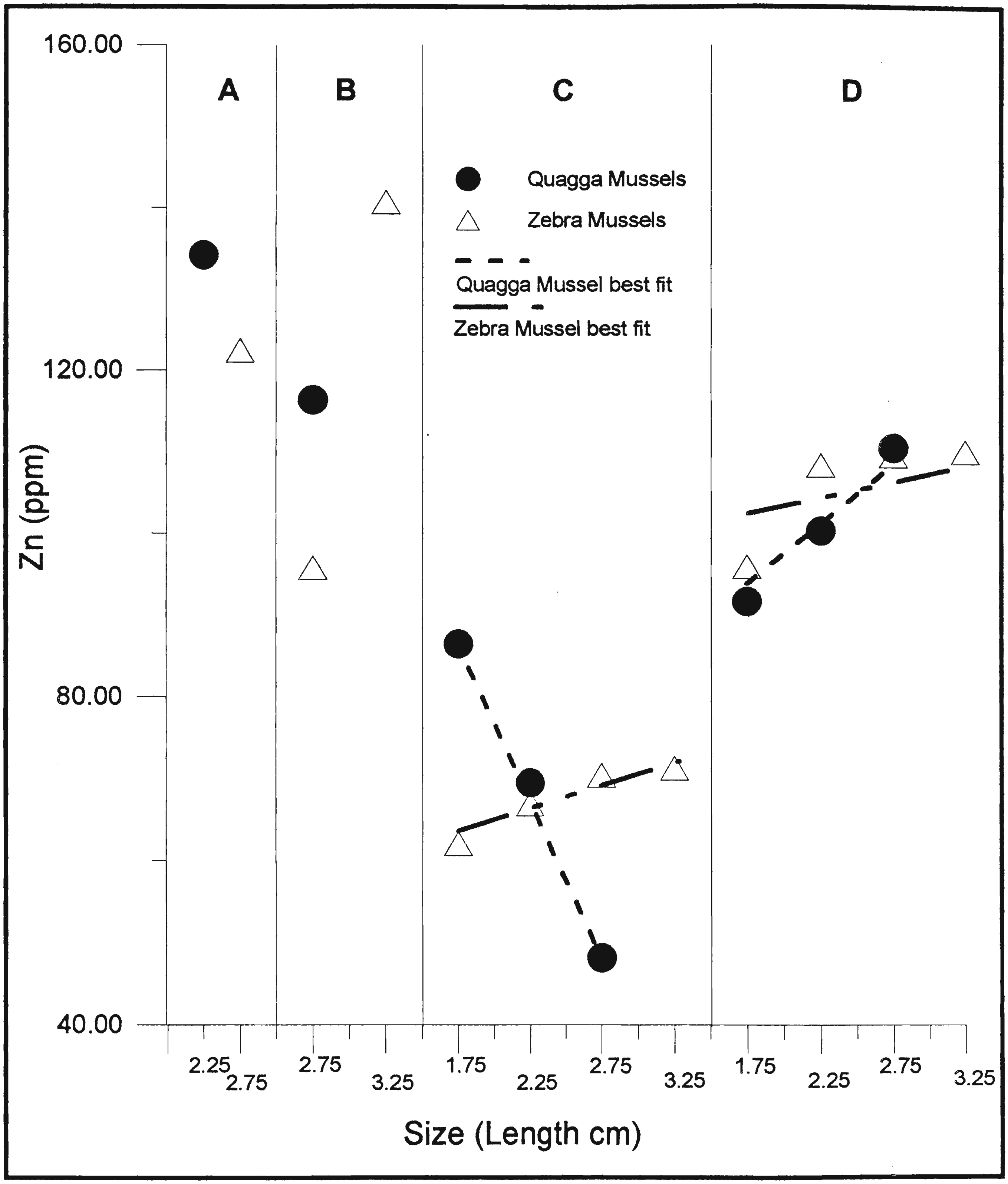


Figure 28: Relationship between Zn (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

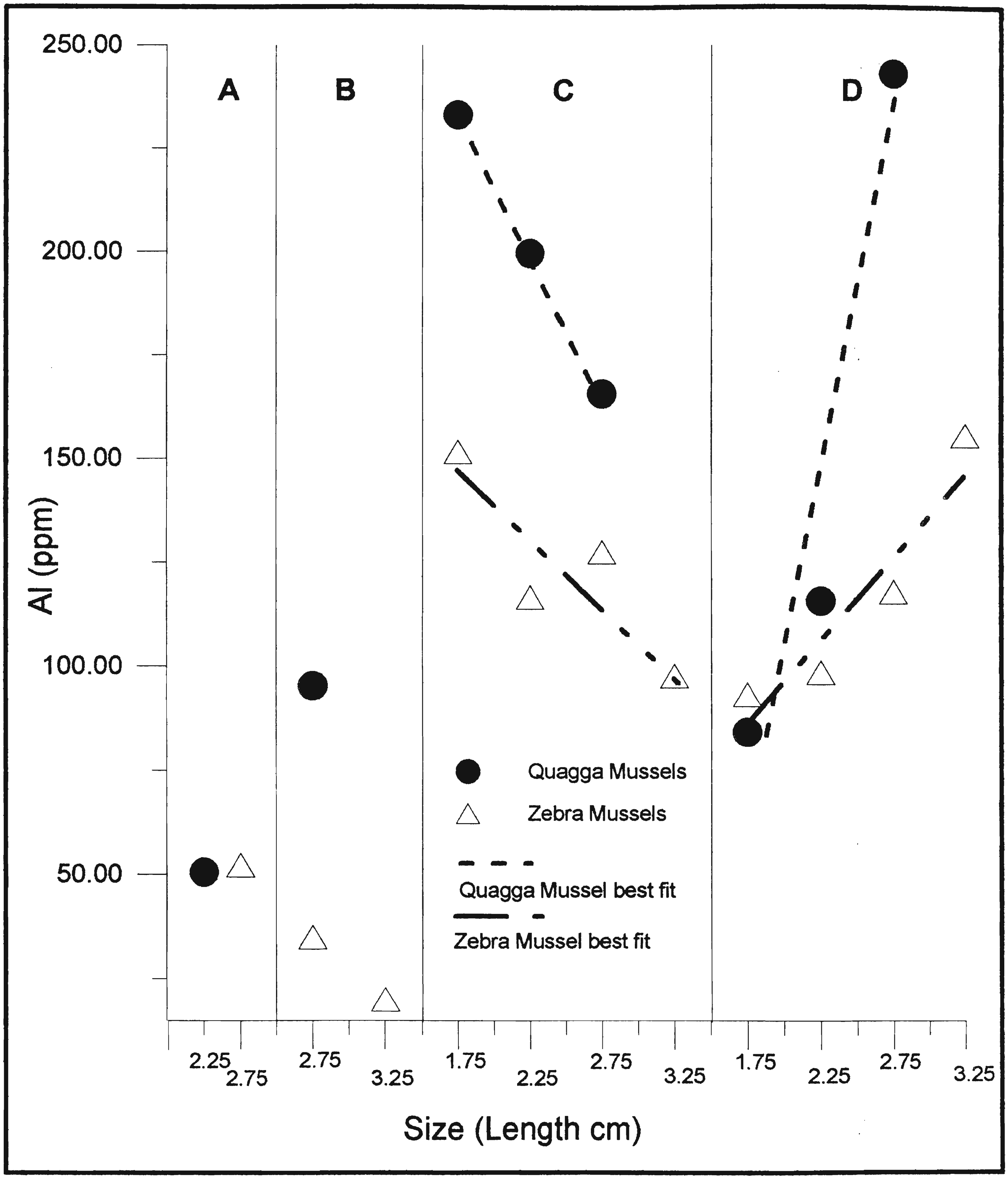


Figure 29: Relationship between Al (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

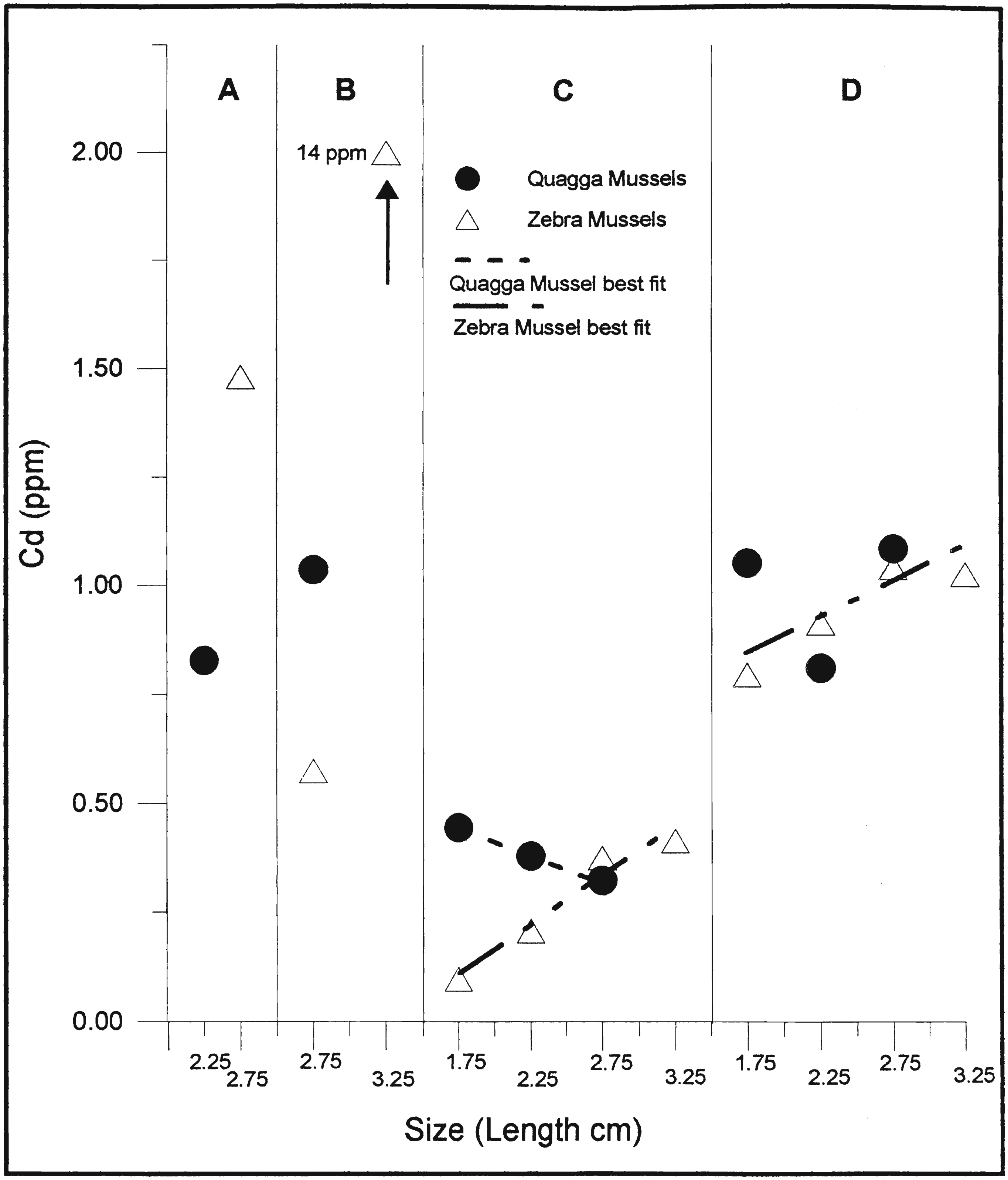


Figure 30: Relationship between Cd (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

Zebra and quagga mussels, Cr content, from Port Colborne and site 10 (Martindale Pond) are similar with about 1 - 1.5 ppm and appear to contain the smallest Cr concentrations (Figure 31). Site 16 zebra mussels seem to have a decreasing Cr trend with increasing size class, whereas the quagga mussels do not seem to have a linear Cr content trend with size class. Zebra and quagga mussels from Lake Gibson appear to have increasing and decreasing Cr trends with size class, respectively, with a greater rate of change in zebra mussel tissue.

Zebra and quagga mussel tissue lead contents are similar with less than 5 ppm. However, the 3.25 cm size class of zebra mussels from site 10 (Martindale Pond) contains about 22.5 ppm of Pb (Figure 32). A similar metal trend was observed in Cd content, and is not ascribed to analytical error. The Pb contents of the specimens from site 16 (Martindale Pond) and Lake Gibson appear to be about the same and do not exhibit any increasing or decreasing Pb trends with increasing size class.

Jeanette's Creek (Lake St. Clair). Only zebra mussels were present at this locality. Four specific size classes (2.25, 2.75, 3.25, and 3.75 cm average lengths) were tested for Cu, Ni, Zn, Cd, Al, Cr, Pb, Co, Be and Mo contents. Of these, the following metals Cu, Ni, Cr, Pb, Co, Be and Mo appear to increase in concentration with increasing size class. In a smaller set, Zn, and Cd seem to decrease with increasing size class. In addition Al contents did not appear to vary with increasing size class.

Specifically, copper content seems to increase steadily from the 2.25 to 3.25 size class, which is followed by a large increase in the next larger size class (Figure 33). Similarly, Ni content also appears to increase in the first three size classes with a steeper rate of change

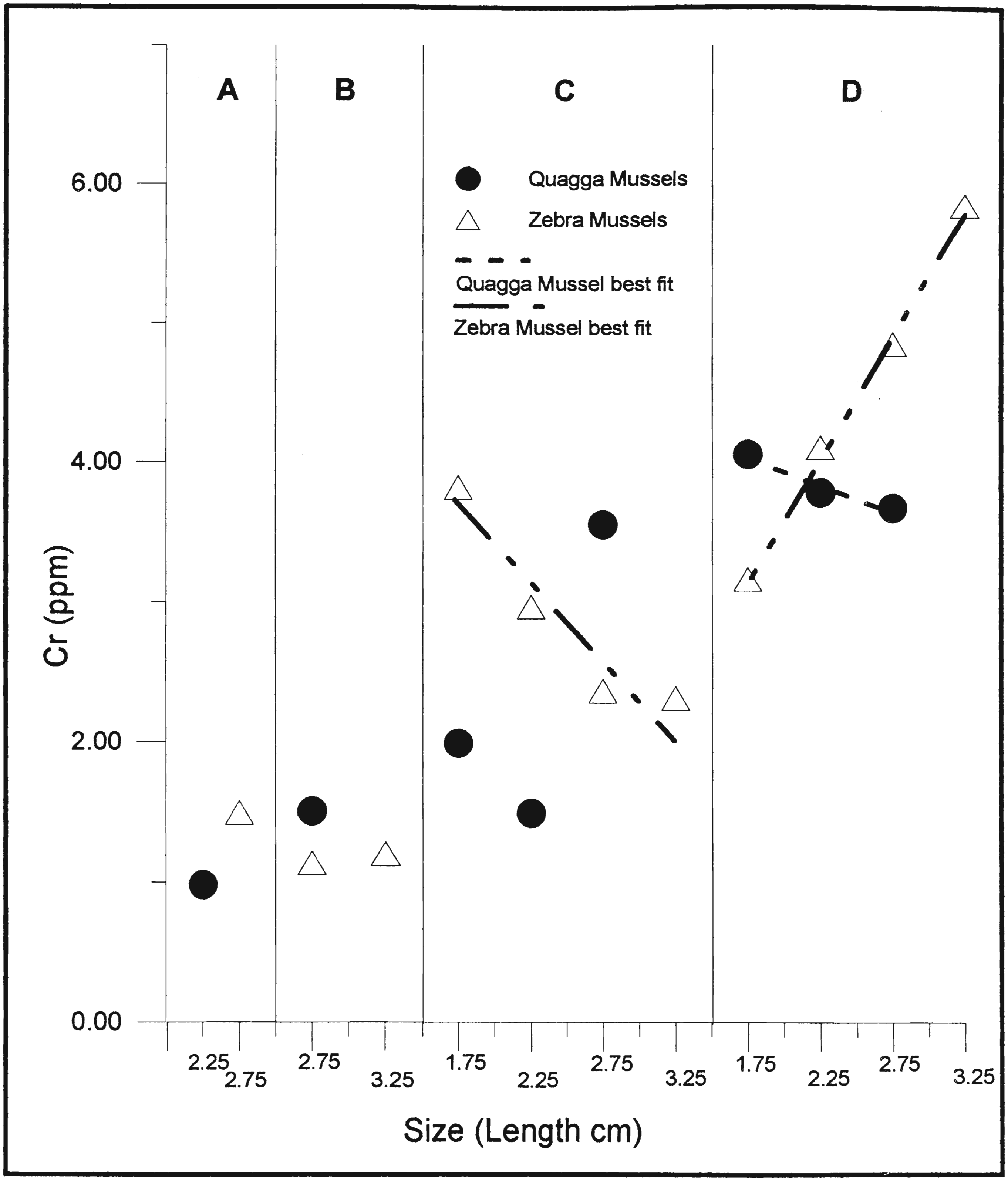


Figure 31: Relationship between Cr (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

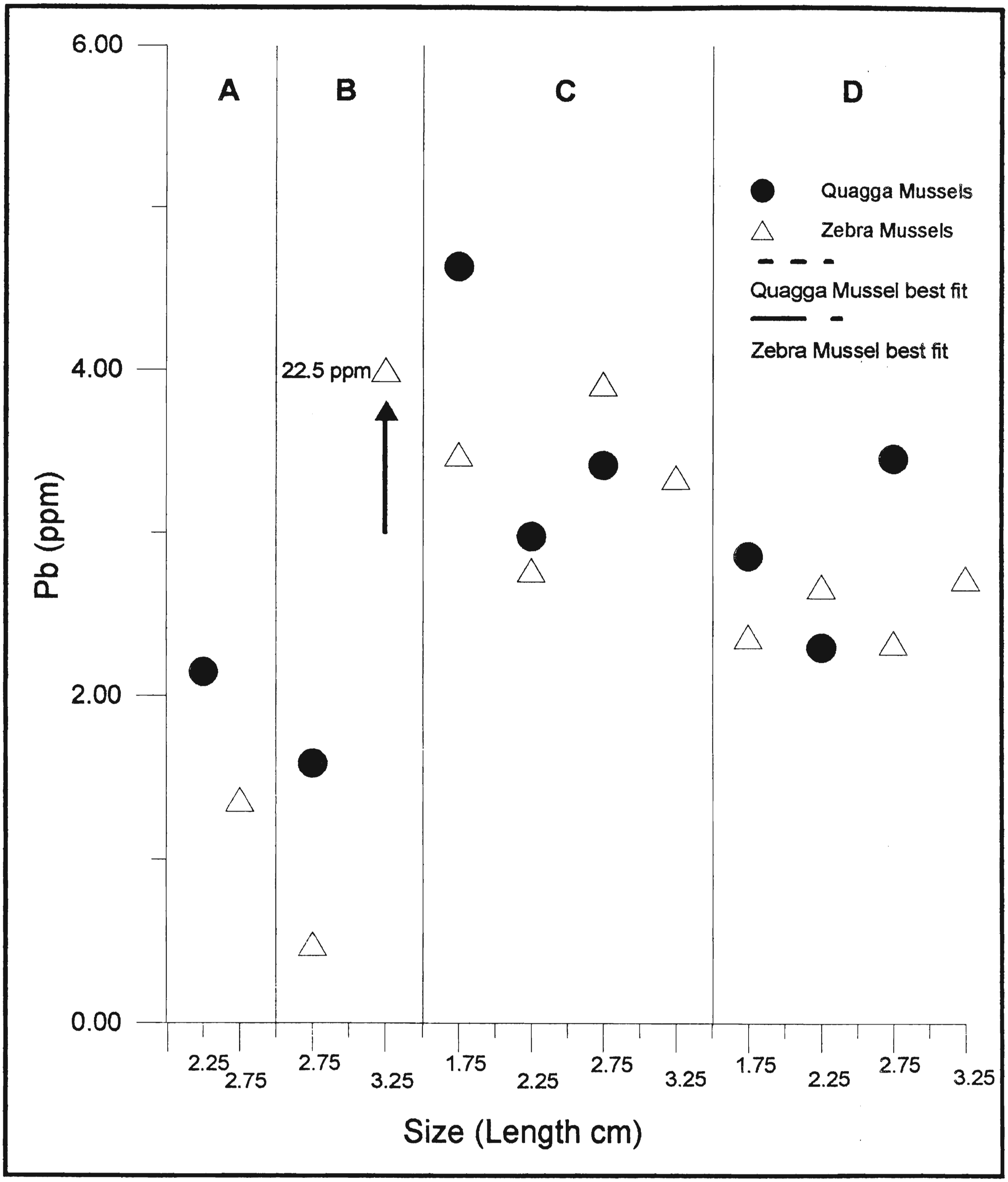


Figure 32: Relationship between Pb (dry weight) and size classes in zebra mussels and quagga mussels from sites A (Port Colborne Harbour), B (Site 10 Martindale Pond), C (Site 16 Martindale Pond), and D (Lake Gibson). Note: 2.75 cm represents mean of 2.5 to 3.0 cm size range.

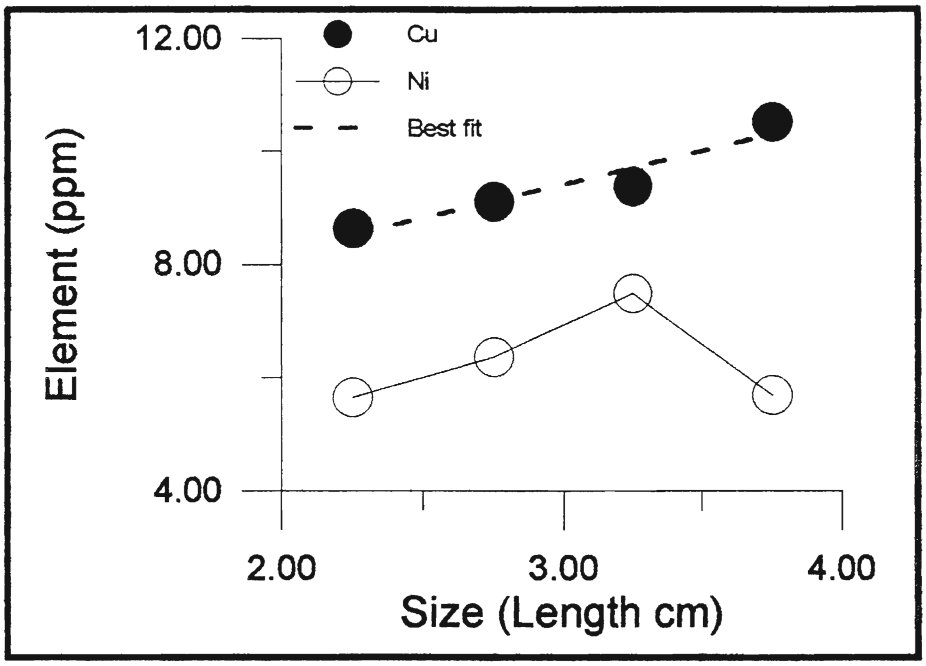


Figure 33: Relationship between Cu, Ni (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

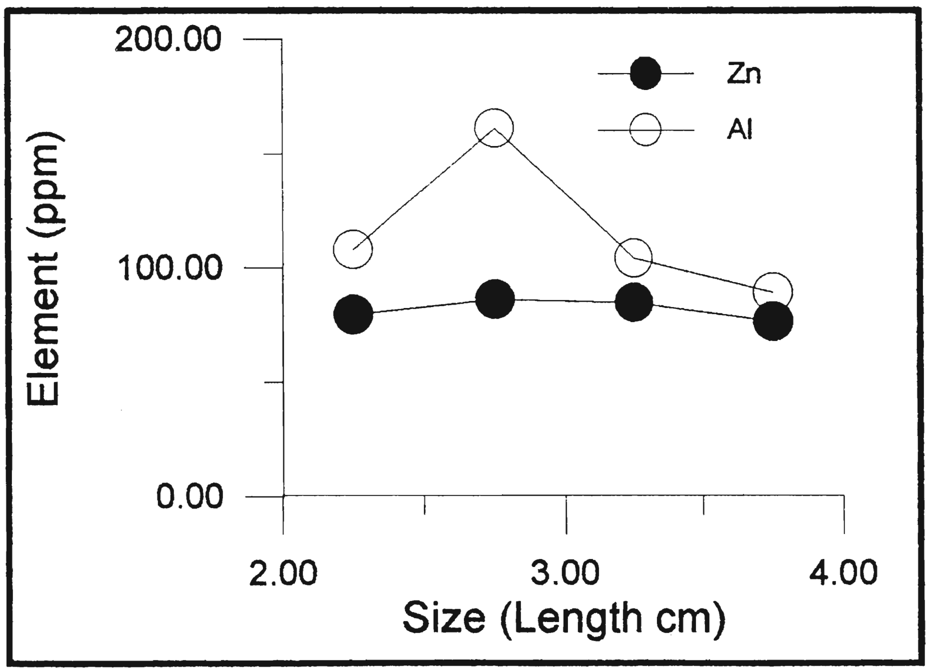


Figure 34: Relationship between Zn, Al (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

than for Cu. This increase seems to be followed by a large decrease in Ni content in the largest of the tested size classes (Figure 33).

Zinc content (Figure 34) seems to gradually increase from the 2.25 to 3.25 cm size class, which is followed by a decrease in the next larger size class. In contrast, Al content (Figure 34) seems to be similar for all size classes, providing a flat Al trend with size class.

Cadmium content, similar to Ni, seems to increase from the 2.25 to 3.25 cm size class (Figure 35). This increase is followed by a decrease in Cd content in the larger of the size classes. Chromium content (Figure 35) appears to increase from the 2.25 to 2.75 cm size class and then decrease in the next two larger size classes.

Lead content (Figure 36) of the various size classes appears to fluctuate and exhibits an overall increase with increasing size class.

Zebra mussel Co (Figure 37) and Be (Figure 38) contents seem to decrease in the first three size classes and are followed by metal content increases in the 3.75 cm size class.

Molybdenum content (Figure 39) appears to slightly decrease from the 2.25 to 2.75 cm size class, which is followed by an apparent increase in the next two larger size classes. Overall, the Mo contents seem to exhibit an increasing trend with increasing size class.

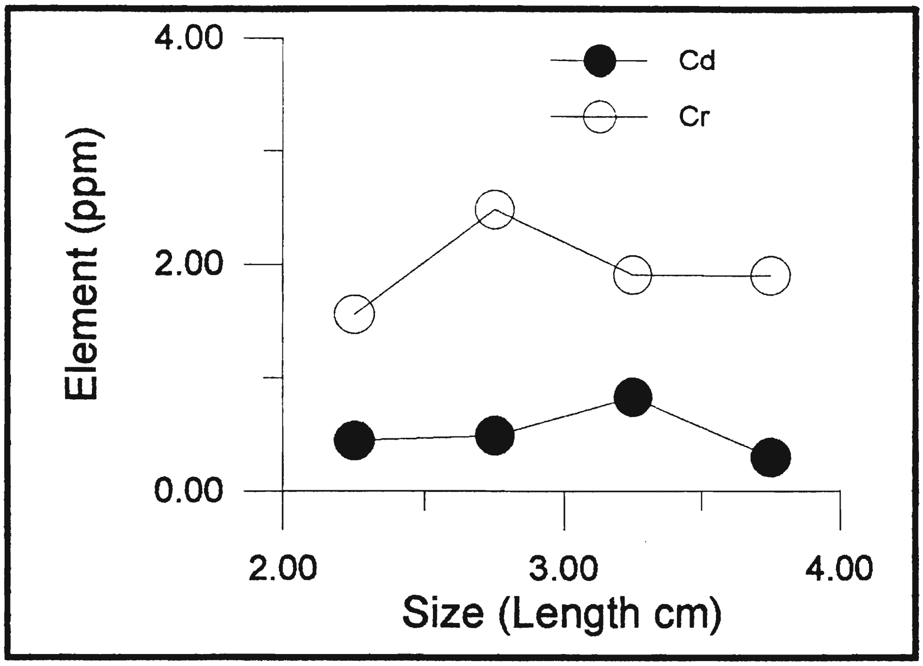


Figure 35: Relationship between Cd, Cr (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

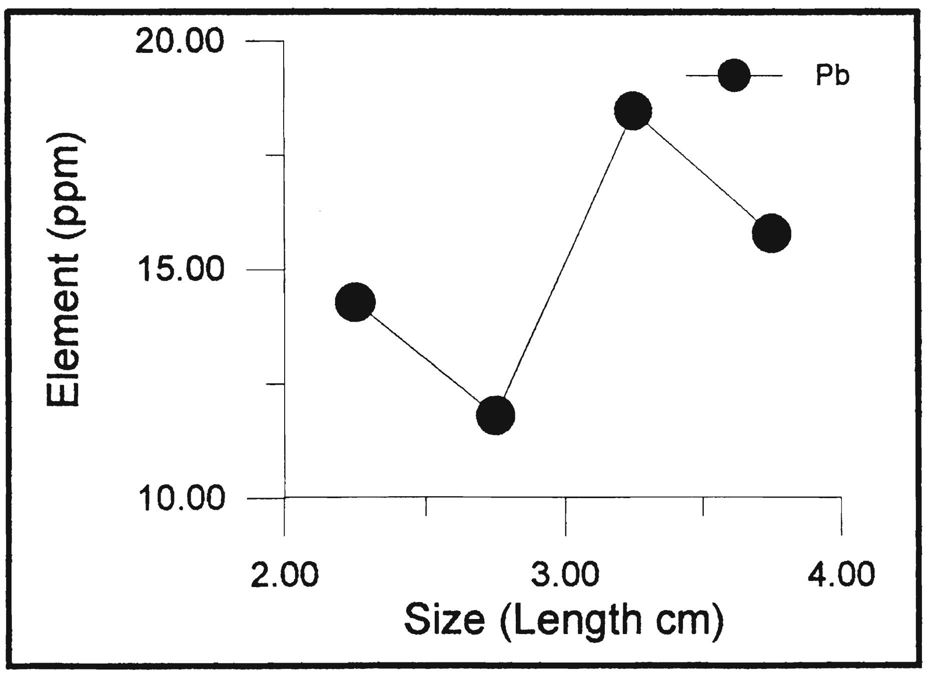


Figure 36: Relationship between Pb (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

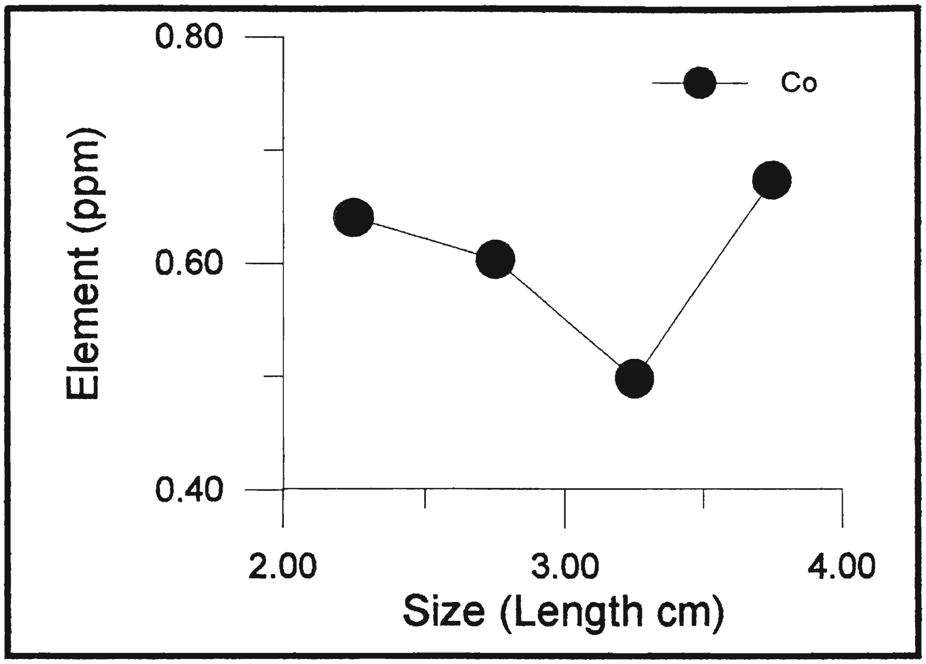


Figure 37: Relationship between Co (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

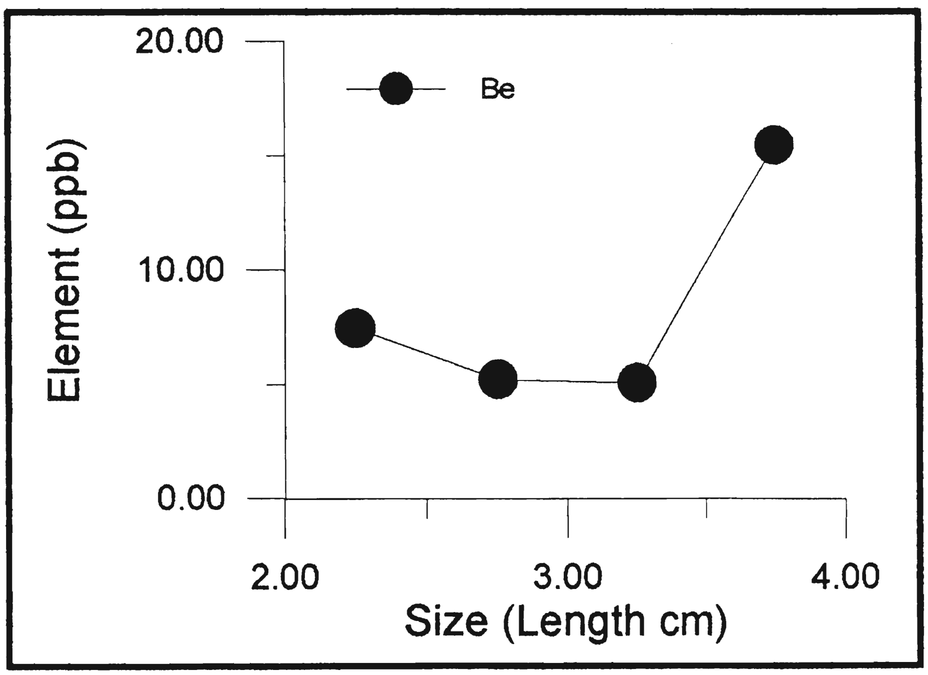


Figure 38: Relationship between Be (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

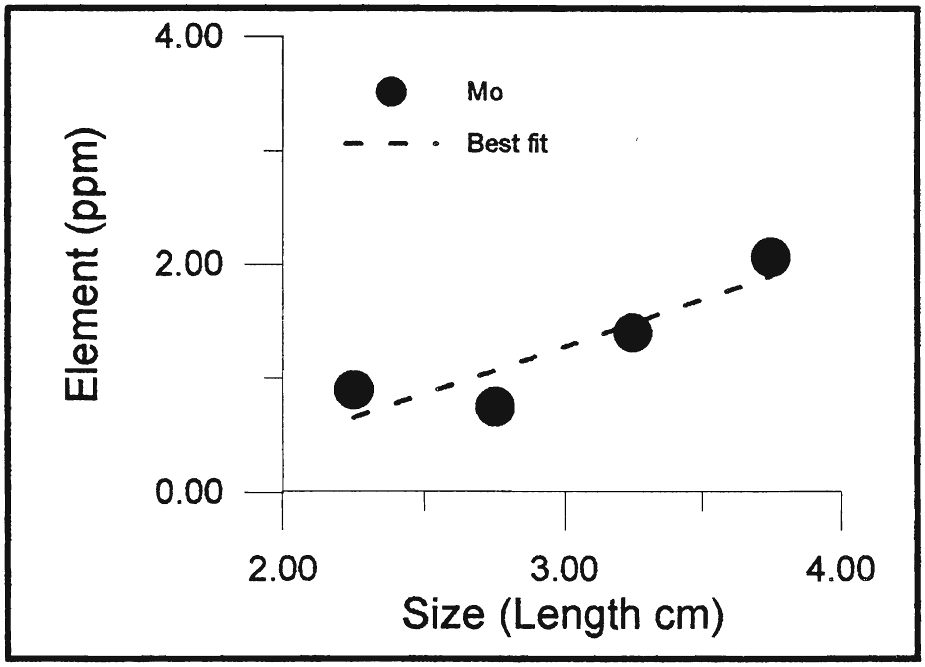


Figure 39: Relationship between Mo (dry weight) and size classes in zebra mussels from Lake St. Clair (Jeanette's Creek, Chatham, Ontario). Note: 2.25 cm represents mean of 2.0 to 2.5 cm size range.

DISCUSSION

Zebra and Quagga Mussel Survey Comparisons

In general, variations in metal concentration with size classes can not be treated as simple bioaccumulation trends. Many factors can influence the trends, such as changes in water chemistry; for example EDTA in the aquatic environment may chelate metals making them unavailable to particular organs within a bivalve and the next generation of molluscs (Hemelraad and Herwig, 1988). One could then easily misinterpret the data as a bioaccumulation trend when in fact the metal is at regulatory concentrations for larger organisms and unavailable to smaller ones. Thus, great caution must be exercised when dealing with multi-size class mollusc-tissue data sets.

High turbidity values were recorded at sampling stations during non-ice covered periods (see **Water Quality**, Chapter 1). However, when ice coverage was extensive, turbidity was greatly reduced. This information suggests that wind induced mixing, in addition to shipping activity, is a considerable parameter in influencing turbidity conditions. Suspended sediments thus may have a great influence on water chemistry (Reeders and Bij de Vaate, 1992).

Mussels in a passive biomonitoring survey in a wind induced environment may be more representative of the general water chemistry than translocated mussels used during an ice-covered period. It is also likely that passive biomonitoring would possibly be more representative of sediment/aquatic chemistry due the longer time period. Some of the essential metals may be regulated up to critical concentrations, which are dependant upon the chemical suite in the organisms, whereas some metals such as Cd (Kraak and Toussiant, 1993) are not regulated.

Cd concentrations in *Anodonta anatina* have been shown to bioaccumulate, while various rates of Cd excretion were observed for particular complexes (Holwerda *et al.*, 1988; Tessier *el al.*, 1993). Since this study does not involve characterisation of complexes or species of metals, only general and magnitude comparisons can be made between sites.

Sedimentation rates are not well known in the study areas, but it is most probable that sediments in the top 10 cm of the column will have the greatest effect on the water chemistry. Zebra mussels in size classes 2 - 3 cm represent about 5 years of growth (Stanczykowska, 1977; MacIsaac, 1994). However more recent studies suggest that zebra mussels in the Great Lakes region rarely live older than 3 years (G. Mackie. per com. 1996). thus the top 10 cm of sediments would be most influential during the mussels life span.

As mentioned in the results section, Cu and Ni concentrations seem to follow linear increases or decreases with mussel size. Zebra mussels sampled at site 10 (Martindale Pond) had an increase for both Ni and Cu over the two size classes. The sediment chemistry also shows an increasing trend over the top 10 cm for both elements (see core total metal MP11; Rowan, 1995). Site 16 (Martindale Pond) zebra and quagga mussels seem to exhibit an inverse Cu tissue relationship with increasing size class. A decreasing Cu concentration trend was also observed in sediments (top 12 cm) at the same location (see total metal MP16, Rowan, 1995). Site 16 quagga mussels seem to display no changes in Ni contents for the various size classes (Figure 27). Similarly, site 16, Ni sediment data (Rowan, 1995), is constant over the uppermost sediment layer. However, Ni content in zebra mussels from site 16 appear to increase with increasing size. This may reflect differential bioaccumulation rates of Ni, in the mussels. Assuming similar growth rates, zebra mussels seemed to accumulate a greater amount of Ni than did quagga mussels and this relationship was consistant for the four sample sites. This suggests that zebra mussels may be better accumulators and thus monitors of Ni contamination than quagga mussels.

Lake Gibson quagga and zebra mussels seemed to have similar Cu and Ni trends. Unlike site 16 (Martindale Pond), both quagga and zebra mussels from Lake Gibson have similar increasing Ni trends in total metal concentration of sediments in cores 37 and 38 (Appendix 1). Cu concentrations (apparent inverse trend) in the mussels does not agree with the increasing upwards trends of the top sediments from cores 37 and 38.

Lake St. Clair zebra mussel Cu concentrations exhibit a direct relationship with size. In contrast, sediments from Lake St. Clair have a decreasing Cu trend towards the sediment/water interface. Ni concentrations from Lake St. Clair mussels have two trends, an increase with size then a drop off. This is not shown in the sediments which have constant concentrations over the top 8 cm and increase downwards to 16 cm. It is obvious that although sediment chemistry reflects some trends in molluscs, the relationship between sediments and organisms is complex.

Quagga mussels sampled from site 16 (Martindale Pond) appear to have inverse Al and Zn trends with size. This is supported by decreasing sediment total Al and Zn content trends in cores 2 and MP16 (Rowan, 1995). Zebra mussels from site 16 had a similar Al trend to the quagga mussels and sediments. However, exchangeable Al concentrations for core 2 sediments, displayed large increases in the top 4 cm. Zn concentrations in the zebra mussels appear to have opposite trends to those of the quagga mussel and sediments. Lake Gibson quagga and zebra mussels seem to have similar relationships between Zn and Al and size, which agrees with increasing total metal sediment trends over the top 10.5 cm in cores 37 and 38. Similar to site 16, Lake St. Clair zebra mussels appear to have no similarities between size class, Zn contents and sediment chemistry. However, like the other groups, Al appears to decrease in organisms from size classes 2.75 cm to larger mussels with a similar relationship between Al values and decreasing sediment depth. Aluminum contents appear to be much higher in quagga mussels than in zebra mussels. This suggests that quagga mussels are probably better accumulators and consequently biomonitors of Al contamination.

Zebra mussels sampled in the Twelve Mile Creek watershed, appear to increase in Cd content with increasing size class. Sediment Cd data are limited to cores 37 and 38 (Lake Gibson), since most values were below detection limits. Quagga and zebra mussel Cd concentrations (Figure 30 and Table 3) were much greater (an order of magnitude) than that of corresponding sediment values. Cd contents in zebra mussels from Lake Gibson seem to slightly increase in Cd content with size of mussel, while quagga mussel contents are relatively constant over the size range. Zebra mussels from site 10 (Martindale Pond) appear to have large increases in Cd for two size classes. Since Cd values were not determined for core MP11 or MP10 (Rowan, 1995), core 4 data were used instead because of its close proximity to cores MP11 and MP10 (Figure 10). The increase in the top 5 cm interval of total Cd sediment concentrations from core 4, which as mentioned above, is similar to trends seen in the zebra mussels. Again Cd, concentrations were greater in the tissues than in the sediments. Site 16 (Martindale Pond) quagga and zebra mussels have Cd concentrations greater than those reported in total Cd concentrations from core 2 sediments. Zebra mussels showed an increase in Cd with size while the inverse was recorded in the quagga mussels. Core 2 sediment data shows an increase in Cd over the top 20 cm horizon. Lake St. Clair zebra mussels also have Cd concentrations that are much greater than the sediment data. In addition, sediment Cd concentrations decrease towards the sediment/water interface, while it appears that zebra mussel Cd contents increased slightly with increasing size class (2.25 - 3.25 cm).

Zebra mussels at site 16 (Martindale Pond) appear to have an inverse size-Cr relationship. Sediment data reported by Rowan (1995) shows an increase in the top sediments (MP10 and MP11). Zebra mussels from Lake Gibson show an increase in Cr content with size. This may be explained by sediment trends from Lake Gibson, where sediments from cores 37 and 38 have increasing total Cr in the top sediments. Quagga mussels from Lake Gibson appear to have inverse Cr trends with size, and non-bioaccumulative trends with sediment data.

No trends were seen for Pb content in zebra or quagga mussel with size at Lake Gibson, site 16 (Martindale Pond), and Lake St. Clair (Figures 32 and 36). Site 10 zebra mussels show a large increase in Pb concentration with size (2.25 - 3.25 cm). Increasing metal contents (top 12 cm) were also found in sediment, as reported by Rowan (1995) in MP10. Core 4 sediments are more representative of inputs from Richardson's Creek and had only a slight increase in Pb over the top 5 cm.

The following table (Table 5) is a ranking from apparent higher to lower metal content in mussel tissues from sites 10 and 16 (Martindale Pond), Lake St. Clair and Port Colborne. Consistent trends for the two size classes of quagga mussels and one size class of zebra mussels were found for Cu, Ni, and Cr at the four sampling sites. Quagga (2.75 cm) and zebra (2.75 cm) mussels have consistent Al trends at the four sites. In addition, Zn and Pb have consistent trends at each of the sample sites.

Histochemical Location

A comparison of specific organs of high metal concentrations follows in Table 6. It appears that *Anodonta* sp. are more similar to zebra mussels in their incorporation and distribution of metals than *Elliptio* sp.

The highest Cu and Ni concentrations are found in the gill tissues of *Anodonta* sp., *Elliptio* sp., and zebra mussels. Heart and rectum and gill organ groups contain the highest Pb content in *Anodonta* sp. and zebra mussels. Both *Anodonta* sp. and zebra mussels had high Zn concentrations in the kidney tissues. *Elliptio* sp. and zebra mussels have high Zn concentrations in heart and rectum tissues. The highest Al concentrations are in the gill and kidney tissues of *Anodonta* sp. and *Elliptio* sp.

Table 5. Locality comparisons by apparent order of metal contents of specific size-class mussels

metal	quagga mussels (2.25 cm)	quagga mussels (2.75 cm)	zebra mussels (2.75 cm)
Cu	Gibs > PtC > 16	Gibs > 16 > 10	Gibs > PtC > 16 > St.C > 10
Ni	PtC > Gibs > 16	Gibs > 16 > 10	PtC > Gibs > 16 = St.C > 10
Zn	PtC > Gibs > 16	10 > Gibs > 16	St.C > PtC > Gibs > 10 > 16
Al	16 > Gibs > PtC	Gibs > 16 > 10	Gibs > 16 > St.C > PtC > 10
Cr	Gibs > 16 > PtC	Gibs > 16 > 10	Gibs > St.C > 16 > PtC > 10
Cd	PtC = Gibs > 16	Gibs = 10 > 16	PtC > Gibs > 10 > St.C > 16
Pb	16 > Gibs > PtC	Gibs = 16 > 10	St.C > 16 > Gibs > PtC > 10

Note: Gibs = Lake Gibson, 16 = site 16 (Martindale Pond), 10 = site 10 (Martindale Pond), St.C = Lake St. Clair (Jeanette's Creek) and PtC = Port Colborne Harbour.

Table 6. Apparent metal content comparison in *Anodonta* sp., *Elliptio* sp., and zebra mussel organ groups.

metal	*Anodonta* sp.	*Elliptio* sp.	Zebra Mussels*
Cu	**Gill**/Kidney	**Gill**	**Gill**
Ni	**Gill**/Kidney	**Gill**	**Gill**
Cd	**Kidney**	Gill/**Kidney**	**Kidney**
Pb	H&R/Gill	Mantle/Kidney	H&R/Gill
Zn	Gill/Kidney	Mantle/H&R	Muscle/H&R/Kidney
Al	Gill/Kidney	Gill/Kidney	ND

Note: * Zebra mussel size class 2.7 - 3.2 cm. *Anodonta* was compiled over 4 size classes, *Elliptio* over 2 size classes, and zebra mussels over 1 size class. **Bold** and Underline represent apparent similar tissue trends for three and two species, respectively.

CONCLUSION

Histochemical analysis and passive biomonitoring using freshwater clams and mussels lead to the following conclusions about the organisms and their biomonitoring potential:

1.. There seems to be a variation in the content of some metals with shell size and between organs. This suggests that size and organ type may be important considerations of biomonitoring studies using bivalves.

2. It appears that a number of divalent metals (e.g., Cu, Ni, and Cd), seem to accumulate preferentially in the gills and kidneys of *Anodonta* sp., *Elliptio* sp., and zebra mussels.

3. Zebra and quagga mussels from Lake Gibson and Martindale Pond tend to have similar Al distribution trends with increasing size class. There seems to be a relationship between sediment contents, Al contents (Chapter 1), and shucked mussel tissue contents.

4. In one instance, zebra mussel soft tissue, Cd content appears to increase with increasing shell size (Martindale Pond and Lake Gibson), whereas in a different watershed (Lake St. Clair, Jeanette's Creek) there seems to be no such trend.

CHAPTER 3

ACTIVE BIOMONITORING

ABSTRACT

Zebra mussel, quagga mussel, *Anodonta* sp., and *Elliptio* sp. were used in a two part, active (translocated) biomonitoring study of the Twelve Mile Creek watershed. There was no statistical difference in death rates between zebra and quagga mussels after 65 days of biomonitoring. However there does appear to be a difference of death rates between sites. Unfortunately the data base did not permit us to differentiate between sites. Relative to Port Colborne Harbour (Port Colborne, Ontario), the Twelve Mile Creek watershed appears to be elevated in bioavailable Al. An area near the terminus of the Twelve Mile Creek appears to be an area of environmental concern since mussels seemed to have accumulated relatively large concentrations of Cd, Zn, and Pb. In addition to possible metal loading from a nearby outfalls, or possible upstream outfalls, road salt runoff from storm sewers may have contributed to metal accumulation through cation exchanges processes. Similar trends in cumulative quagga mussel metal concentrations during the two time periods (65 and 159 days), suggest that quagga mussels may reach equilibrium within 65 days of translocation. Differences in bioaccumulated metal concentrations of the two dreissenid species demonstrate that active biomonitoring studies must use a variety of organisms to adequately assess the environmental situation of specific waterways and/or bodies.

INTRODUCTION

There are many factors that contribute to metal accumulation and depuration in organisms. Single metal toxicity tests, while informative for histochemical location, may not be valid in the natural or anthropogenic impacted environment. Metals may compete for binding sites in the tissues and the process may be neutral, synergistic or antagonistic. Equitoxic mixtures of Cu, Cd, and Zn are toxic in zebra mussels at levels below the no effect concentration (NOEC) values for each of the metals (Kraak and Lavy, 1993). Tessier *et al.* (1984) demonstrated a competitive nature, for binding sites, in *Elliptio complanata* between Fe, Cu, Pb, and Zn, and suggested that Fe oxyhydroxides in competition with organics control the toxic effects of Cu, Pb, and Zn. *Anodonta grandis* showed no correlation between amorphous Fe complexes or organic compounds to Cd accumulation (Tessier *et al.*, 1993). Additions of EDTA have been shown to reduce Cd accumulation by a factor of 3 (Holwerdra *et al.*, 1988). There are many factors influencing the accumulation of metals and their toxic effects in organisms.

Relationships between metals exist and Puymbroeck *et al.* (1982) demonstrated a mutually antagonistic accumulation effect for Cd and Se. In the presence of Zn, uptake of Cd by *Anodonta cygnea* was halved. Metallothionein and metallothionein-like-protein and additional lysosome production was enhanced in the epithelia cells of the kidney by the addition of Cd. This is believed to have enhanced the accumulation of Zn by adding binding sites in gill's and kidney's. Similarly, de Kock and Bowner (1993) reported large Cd and Zn concentrations in zebra mussels after an industrial Cd spill. In addition, *Anodonta cygnea,* when exposed to lethal concentrations of Cd, showed no accumulation effects for Al, Be, Co, Cr, Cu, Mo, Ni, or Pb (Hemelraad and Holwedra, 1990). Similar studies of this nature should be used to set water/sediment parameters and monitor waterways, because accumulation in one trophic group such as the exploitive quagga and zebra mussels will ultimately end up transferring contaminants to a higher trophic level (de Kock and Bowner, 1993).

In addition to building a database of sediment and organism health (Chapters 1 and 2) the aim of the third part of the study, using active (translocated) biomonitors, is to test the feasibility of using different bivalves as biomonitors. It is hoped that tissue metal concentrations will add to the database and help in identifying areas of environmental concern. Furthermore, it is hoped that, with future work, such a database will aid in assessing the effectiveness of passive (indigenous) to active bivalve biomonitoring surveys.

Field Biomonitoring Procedures

Zebra and quagga mussels used for the active biomonitoring survey were sampled from Port Colborne Harbour (Lake Erie), and are a subset of the sample group used for passive biomonitoring. Zebra and quagga mussels, and native clams were placed into stainless steel cages and placed in areas also used in the passive biomonitoring survey (Chapter 2). Active biomonitoring was initiated on November 9/94, well after the spawning season of both dreissenid species. A cage was placed in Short Hills Provincial Park (SHPP) near site 34A, which contained only native fresh water clams (*Anodonta* sp. and *Elliptio* sp.) to prevent headwater contamination by zebra and quagga mussels. Zebra and quagga mussels used in the study did not spawn in the laboratory holding tank before use, even after raising the water temperature to induce spawning. Zebra and quagga mussels spawn last in late August to mid

September (Stanczykowska, 1977; Borcherding, 1991). To avoid that, our mussels were sampled in mid October. Zebra mussels of 2.5 to 3 cm and quagga mussels of 2 to 2.5 cm were used in this study. A summary of cage content follows (Table 7).

Table 7. Cage Contents and sizes of mussels used in the active biomonitoring survey (November 9/94).

Locality	Zebra Mussels 2.5 - 3.0 cm	Quagga Mussels 2.0 - 2.5 cm	*Elliptio* sp. variable*	*Anodonta* sp. variable*
Lake Gibson[a]	29	60	0	3
SHPP[b]	0	0	2	1
Decew Falls (32)	29	60	1	2
Glendale Ave. (30)	29	60	0	3
Niagara College	29	60	1	2
Capri (22)	29	60	0	3
Lookout Point[c]	29	60	1	2
Rennie Park (2)	29	60	1	2

[a] 100 m west of site 37. [b] 50 m west of site 34A. [c] Rowan (1995) site 10 near storm sewer S14 (Martindale Pond; Figure 2). * see Appendix 3.

A cage was placed 100 m west of site 37 in Lake Gibson (Figure 4, Chapter 1). The SHPP cage was placed 50 m downstream of site 34A (Figure 3). Decew Falls cage was placed in Twelve Mile Creek directly across from site 32 (Figure 5B). Glendale Avenue cage was placed 10 m downstream of site 30 (Figure 5C). Niagara College cage was placed 100 m upstream of site 1cr (Rowan, 1995). Capri cage was placed 5 m south of site 22 in

Martindale Pond (Figure 9). Lookout cage was placed 30 m north of site 10 (MP11 Rowan, 1995; Figure 10). Rennie Park cage was placed approximately 30 m east of site 2 and called site 16 (Figure 10).

All cages, made of stainless steel (10 x 10 x 30 cm), were placed on the substrate and tied off with string. Cage contents were examined after two time periods. After 65 days (January 13/95) all zebra mussels and 30 of 60 quagga mussels were removed from each cage. Subsequently, cages were placed back into the water, and the second stage of biomonitoring continued until April 7/95 (159 days in total), when the cages and their contents were removed from the water.

The 65 day period was assumed to be sufficient time for both zebra and quagga mussels to accumulate contaminants, because zebra mussels approach equilibrium conditions with ambient water chemistry within 40 to 60 days (de Kock *et al.*, 1993). Thus, the zebra mussels should have reached equilibrium with any bioavailable metal. No work on biomonitoring using quagga mussels has been reported. Two stages of biomonitoring were used to determine how much time is required for these mussels to reach equilibrium. It was assumed that a period of 159 days would be sufficient for unionids and quagga mussels to attain equilibrium.

The fall and winter months are particularly a good time for translocation experiments because the spawning season is over (Borcherding, 1991), and thus associated weight loss will not affect tissue metal concentrations. In addition, mussels spend most of their energy in maintaining their metabolic activity and in gametogenesis. A disadvantage is that during the winter months absorption of nutrients from unused gonads may occur (Mersch and Pihan, 1993; Sprung and Borcherding, 1991; Borcherding, 1991) if food supply is insufficient to meet crucial energy requirements for gametogenesis. The winter of 94/95 was unseasonably mild with numerous thawing and freezing periods. This prolonged the autumn-like conditions, and probably provided ample food during the winter season..

Cages placed into Twelve Mile Creek, in particular at Decew Falls, Glendale, and Niagara College, were located in bottom areas protected from the otherwise fast flowing current. The reason for this was two fold; to locate the mussels in regions where extensive zebra mussel colonies were seen at times of low flow and to remove the more sensitive clams from the faster (very turbulent) flowing waters which carry more coarse material, known to irritate bivalve siphons. This may reduce filtering activity, and lead to death of both mussels and clams (Stanczykowska, 1977; A. H. Houston pers. com. 1994).

METHODS

Tissues

Zebra and quagga mussel tissues were pooled and dissection and digestion were performed as described in Chapter 2. Due to the small number of unionids used, organ specific concentrations, are not discussed in the text, but are reported in Appendix 3 to aid future studies. Zebra and quagga mussel concentrations are also reported in Appendix 3. Elemental weight ratios were calculated by dividing the analytical concentrations of samples by those of the reference mussel material (Chapter 2). This format permits quick assessment of metals accumulated in the mussel tissues during biomonitoring surveys. In addition, it facilitates inter metal comparison content to reference values and aids in the identification of areas of environmental concern.

Statistical analyses of zebra and quagga mussel survival during both periods were performed using the Minitab 8 program. Due to the small population size of the large clams used in the study, *Anodonta* sp. and *Elliptio* sp., statistical analyses of death rates were not possible (E. Mueller, pers. com. 1995). Paired Wilcoxian tests were used to determine whether death rates between zebra mussels (65 days) and quagga mussels (65 days), and between both quagga mussel groups (65 days and 159 days) were different at the 95% confidence level. Chi^2 tests were used to determine whether there was a significant difference in death rates at the specific localities for the zebra and quagga mussel (65 day) population, and the quagga mussel (65 day and 159 day) populations. Finally, confidence interval tests (at the 95% level) were performed on the zebra and quagga mussel (65 day) population, and the quagga mussel (65 day and 159 day) populations to determine which site, or sites, were not conducive to mussel survival.

RESULTS

Mussel statistics

***Anodonta* sp.** Translocated *Anodonta* sp. were measured in the laboratory before translocation and after the 159 days of biomonitoring. Growth measurements are summarized in Table 8. All mussels except for one of two at Capri (22A) site, grew in either lengths and/or breadths. This demonstrates that these mussels had actively fed and filtered water during the survey period.

Table 8. Growth Rates after 159 days for translocated *Anodonta* sp.

	Length (mm)			Breadth (mm)		
Location	Day 1 (Nov. 9/94)	Day 159 (Apr. 7/95)	ΔL	Day 1 (Nov. 9/94)	Day 159 (Apr. 7/95)	ΔB
SHPP	100	101	1.0	38.0	38.5	0.5
Lake Gibson	132	132	0	49.5	51.0	0.5
Decew Falls	104	104.5	0.5	46.5	47.5	1.0
Niagara College	105	106	1.0	40.0	42.0	2.0
Capri (22A)*	**118**	**118**	**0**	**52.0**	**52.0**	**0**
Capri (22B)*	108	109	1.0	41.0	41.5	0.5
Site 10 (MP)	109	110	1.0	47.5	47.5	0
Site 16 (MP)	113.5	114	0.5	42.5	43.0	0.5

* A and B refer to different clams. ΔL - change in length, ΔB - change in breadth.

***Elliptio* sp.** *Elliptio* sp. were treated in the same manner as *Anodonta* sp. Growth measurements are summarized in Table 9. All mussels displayed significant growth. Only the large clam used at site 16 (Martindale Pond) did not grow in breadth. Since the clams displayed growth, it indicates that they must have actively filter fed throughout the biomonitoring period.

Each time (65 days and 159 days) bivalves were retrieved from their respective cages, the number of dead individuals was noted for each bivalve group. A summary of mortality rates can be found in Table 10.

Table 9. Growth rates after 159 days for translocated *Elliptio* sp.

Location	Length (mm)			Breadth (mm)		
	Day 1 (Nov. 9/94)	Day 159 (Apr. 7/95)	ΔL	Day 1 (Nov. 9/94)	Day 159 (Apr. 7/95)	ΔB
SHPP A	91.5	92.0	0.5	35.0	35.5	0.5
SHPP B	90.0	91.0	1.0	33.0	36.0	3.0
Niagara College	91.0	92.0	1.0	40.5	42.0	1.5
Site 16 (MP)	115.0	117.0	2.0	42.0	42.0	0

Note: ΔL - change in length. ΔB - change in breadth.

Table 10. Bivalve death rates (dead/initial number).

Bivalve	SHPP	L.G.	D.F.(32)	Glen(30)	N.C.(1)	Cap(22)	Site 10	Site 16
Zm[a]	N.A.	2/29	10/29	14/29	4/29	10/29	3/29	1/29
Qm[a]	N.A.	4/30	10/30	3/30	4/30	0/30	1/30	1/30
Qm[b]	N.A.	3/30	10/30	4/30	6/30	30/30	3/30	2/30
Ano[a]	0/3	1/3	0/3	1/3	0/2	0/3	0/2	0/2
Ano[b]	0/1	2/3	1/2	2/3	1/2	1/3	1/2	1/2
Ell[a]	0/2	N.A.	1/1	N.A.	0/1	N.A.	0/1	0/1
Ell[b]	0/2	N.A.	N.A.	N.A.	0/1	N.A	1/1	0/1

Note: [a] 65 day period. [b] 159 day period. Zm = Zebra mussel, Qm = Quagga mussel, Ano = *Anodonta* sp., Ell = *Elliptio* sp., L.G. = Lake Gibson, D.F.(32) = Decew Falls (32), Glen(30) = Glendale Avenue, N.C.(1) = Niagara College (1), Cap(22) = Capri (22), S10 = Site 10 (Martindale Pond), S16 = Site (Martindale Pond), N.A. = not applicable

Paired Wilcoxian Test

Using data in Table 10, paired Wilcoxian tests at the 95% confidence level confirmed that the null hypothesis, that their death rates are the same could not be rejected for either zebra (65 days) and quagga mussel (65 days) groups or quagga (65 days) and quagga (159 days) mussel groups. Similarly, paired Wilcoxian tests were performed on the same groups at the 90% confidence level. The null hypothesis could not be rejected for the quagga mussel groups (65 and 159 days). However the null hypothesis was rejected for zebra (65 days) and quagga (65 days) mussel groups. Test results are summarized in Table 11.

Table 11. Paired Wilcoxian statistics.

	N	Estimated Median	Achieved Confidence	Confidence Interval
Zm and Qm [a] (95%)	7	0.056	94.8	(-0.030 , 0.345)
Qm [b] (95%)	7	-1.3	94.8	(-16.00 , 0.0)
Zm and Qm [a] (90%)	7	0.056	89.2	(0.001, 0.207)
Qm [b] (90%)	7	-1.3	89.2	(-15.50 , 0.0)

[a] Zebra and quagga mussels (65 days). [b] Quagga mussels (65 and 159 days).

Chi^2 Tests

Since the paired Wilcoxian tests show that the four groups tested were indistinguishable at the 95% level, they were subsequently treated as two populations. In order to test whether mortality rates are different, an average mortality rate was calculated for the two populations (zebra and quagga mussels used for 65 days, and quagga mussels used for 65 and 159 days). Subsequently a Chi^2 test was performed, comparing the average mortality (zebra and quagga mussels for 65 day period had an average site mortality of 9.57, and quagga mussels for 65 days and 159 day periods had an average mortality of 11.57) against the site specific mortalities. The zebra and quagga mussels (65 days), and quagga mussels (65 days and 159 days), had Chi^2 values (27.974 and 50.624, respectively) which are greater than the 95% confidence Chi^2 cutoff at 6 degrees of freedom with 12.592. Therefore, the null hypothesis, that their site specific death rates are the same, was rejected in both cases.

Confidence Interval Tests

Because there was a difference in the site death rates, it was deemed prudent to determine which, if any, specific site(s) is responsible for the rejection of the Chi^2 null hypotheses presented above. Due to the difference in group size between quagga and zebra mussels (30 and 29, respectively), mortality means (rates) were normalized. Likewise, for continuity, quagga mussel (65 days) and quagga mussel (159 days) means (rates) were also normalized. Means and two tailed 95% confidence intervals were calculated to test for mortality means at each site of both populations in comparison to their overall mortality means. The results are summarized in Table 12.

Confidence intervals (95% level) about each site's mean, in the zebra mussel and quagga mussel 65 day mortality rate overlap (Figure 40). Similarly, the confidence intervals of the quagga mussel population (65 days and 159 days) mortality rate means also overlap (Figure 41), however to a lesser degree.

Table 12. Population mortality means (rates) and 95% confidence intervals at each site.

	Zm (65) and Qm (65)[a]			Qm (65) and Qm (159)[b]		
	Mean rates	Lci[c]	Uci[d]	Mean rates	Lci[c]	Uci[d]
Lake Gibson	0.102	0.0246	0.1788	0.117	0.0354	0.1979
Decew Falls (32)	0.339	0.2182	0.4598	0.333	0.2141	0.4526
Glendale (30)	0.280	0.1726	0.4056	0.177	0.0354	0.1979
Niagara College (1)	0.136	0.0482	0.2230	0.167	0.0724	0.2610
Capri (22)	0.170	0.0738	0.2652	0.500	0.3735	0.6265
Site 10 (M.P.)	0.068	0.0036	0.1319	0.067	0.0035	0.1298
Site 16 (M.P.)	0.034	0.0000	0.0810	0.050	0.0000	0.0810

Note: [a] Population of both quagga and zebra mussels at 65 days. [b] Population of both quagga mussel groups (65 and 159 days). [c] Lower confidence interval. [d] Upper confidence interval.

Tissue Chemistry

Zebra mussels. As mentioned in the methods section, concentrations of zebra mussels involved in the survey were divided by those not used in the monitoring process to derive unitless ratios (Appendix 3).

Cu content in zebra mussels from Lake Gibson seem to have increased relative to the reference mussels, while all other areas showed a decrease (Figure 42). The Capri (site 22) mussels had Cu concentrations similar to the original concentrations of the Port Colborne reference collection.

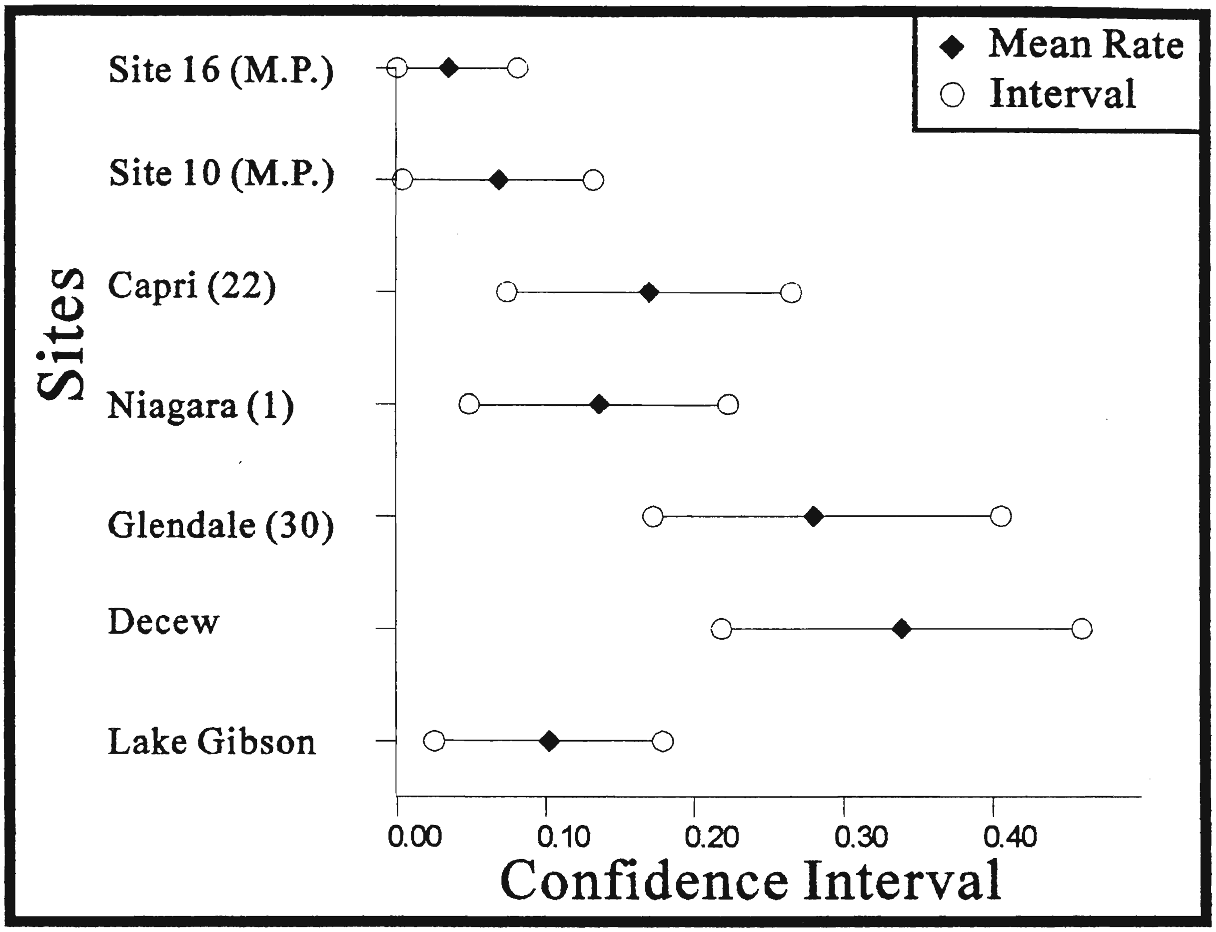


Figure 40: Two tailed confidence interval testing (at 95%) of site specific, quagga and zebra mussel population death rates (65 days).

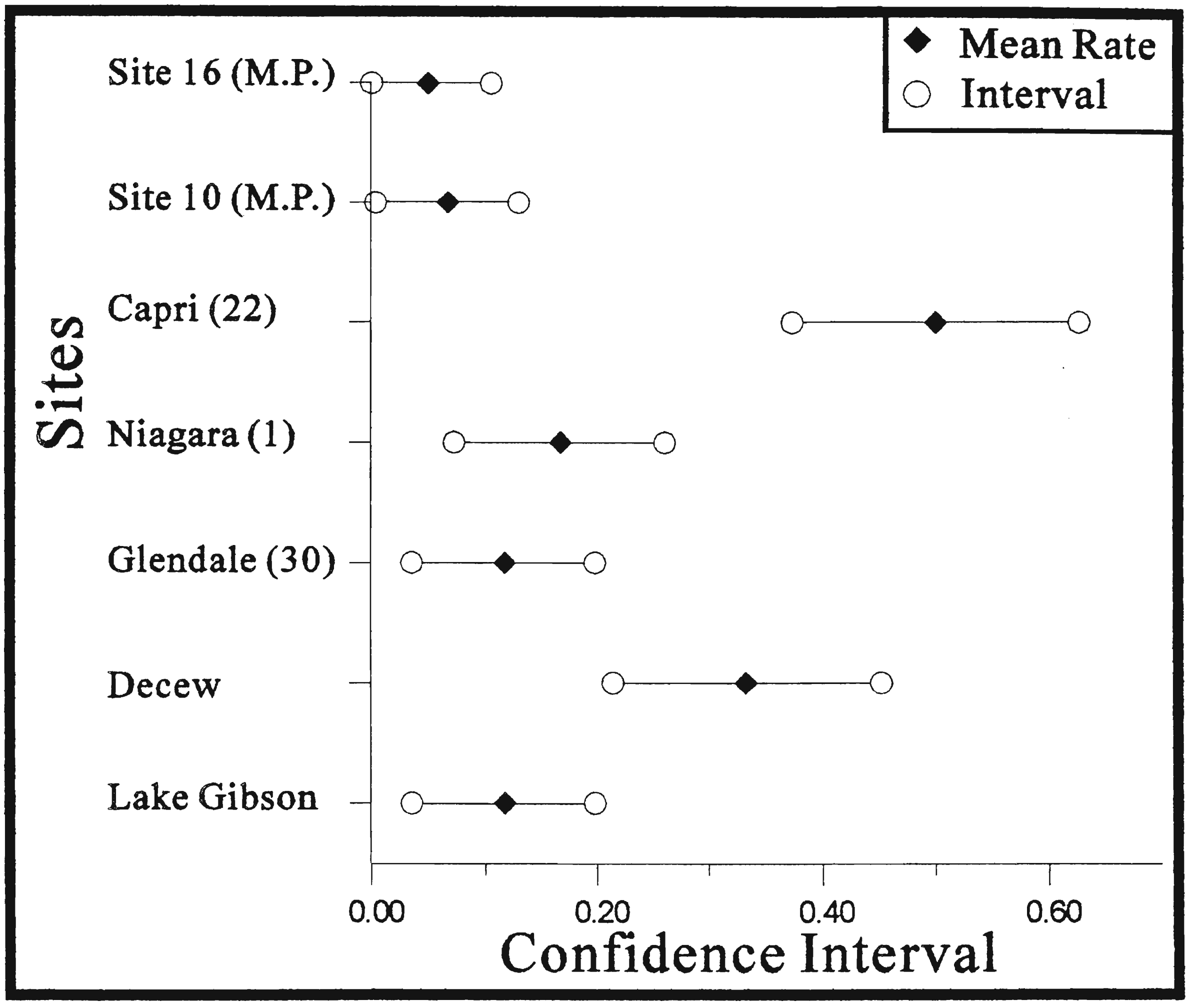


Figure 41: Two tailed confidence interval testing (at 95%) of site specific, quagga mussel population, death rates (65 and 159 days).

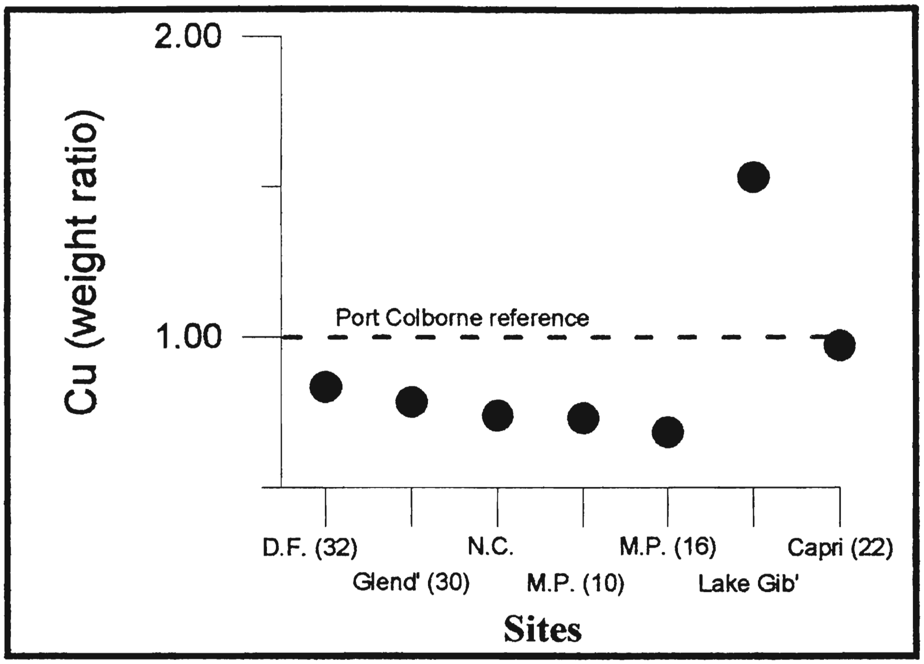


Figure 42: Cu dry weight ratios of zebra mussels from the sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

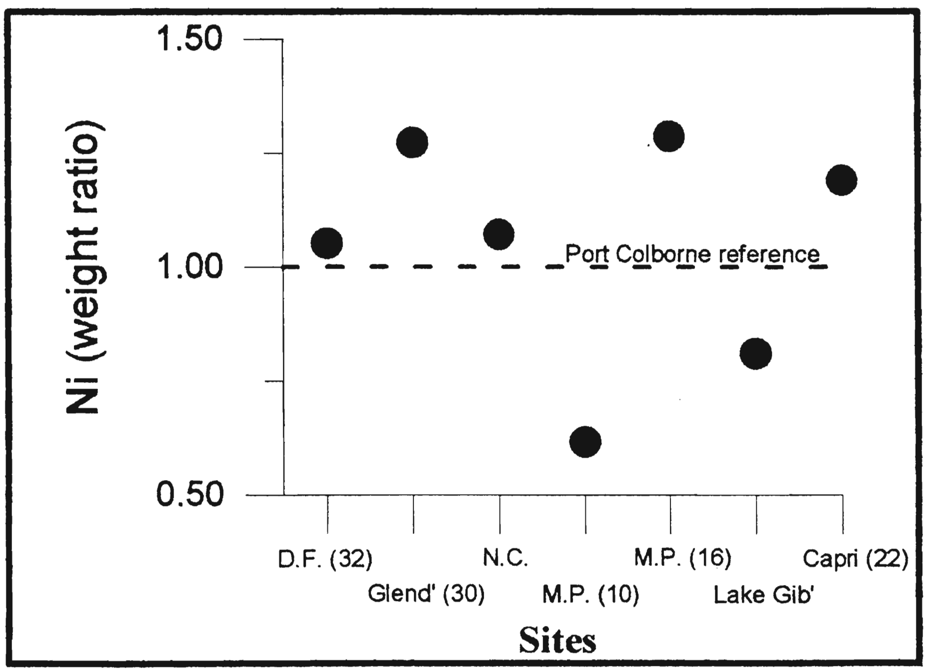


Figure 43: Ni dry weight ratios of zebra mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

At site 10 (Lookout Park; Martindale Pond) and Lake Gibson, the zebra mussel biomonitors seemed to have had reduced Ni concentrations (Figure 43), while the other areas had elevated Ni values. The greatest increases occurred at Glendale (site 30) and Site 16 (Rennie Park, Martindale Pond). Mussels in cages from the Decew Falls and Niagara College location had values similar to those of the reference concentrations.

The greatest Cd concentration increase appears to have occurred in specimens translocated at Decew Falls (Figure 44), and the next highest was found at Capri (site 22). Glendale (site 30) and Niagara College station mussels had Cd values similar to the original concentrations, whereas those from sites 10 and 16 showed reductions in their respective Cd contents.

Mussels from all biomonitoring sites seemed to record increased levels of Al (Figure 45). The 20 times increase observed for the Decew Falls site mussels is exceptionally high. The next highest increases were found, in decreasing order, in mussels positioned at Glendale (site 30), Martindale Pond (site 10), and Capri (site 22) in decreasing order. Lake Gibson mussels recorded the lowest increase in Al content, although all test groups were higher in Al than the reference population.

The Cr values (Figure 46) appear to have increased in the organisms used at six stations, except the Niagara College site which had a ratio just below 1. Mussels used at Decew Falls were also similar to the original reference concentrations. The greatest increases in Cr were measured in zebra mussels from cages deposited at sites 10 and 16 (Martindale Pond).

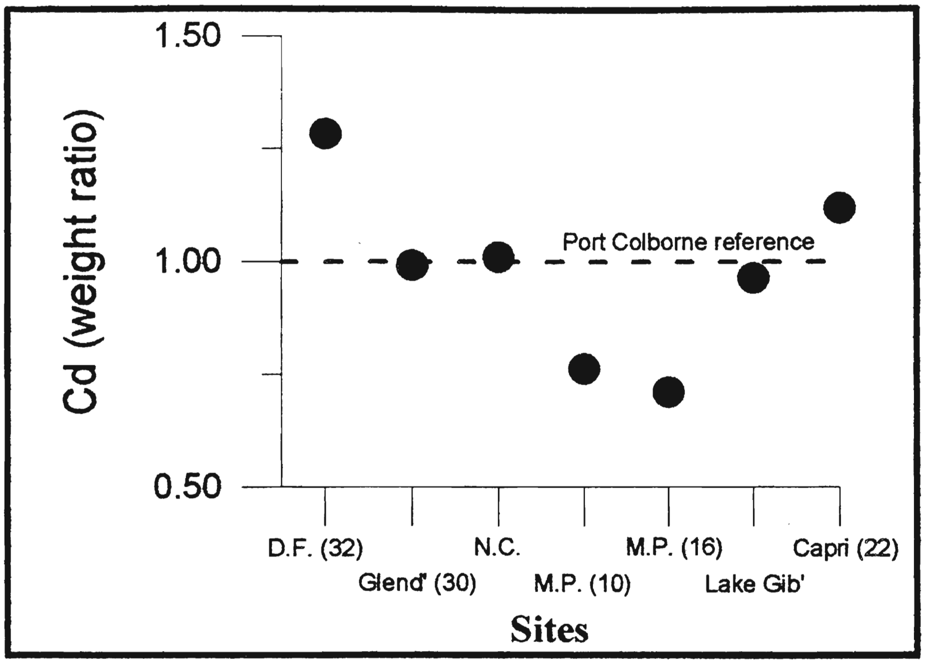


Figure 44: Cd dry weight ratios of zebra mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

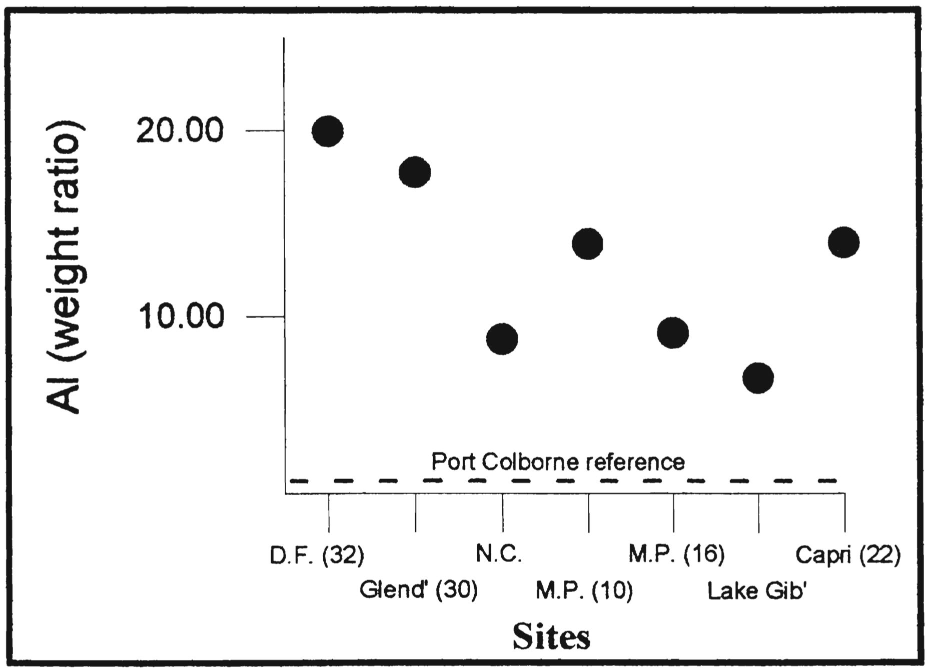


Figure 45: Al dry weight ratios of zebra mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

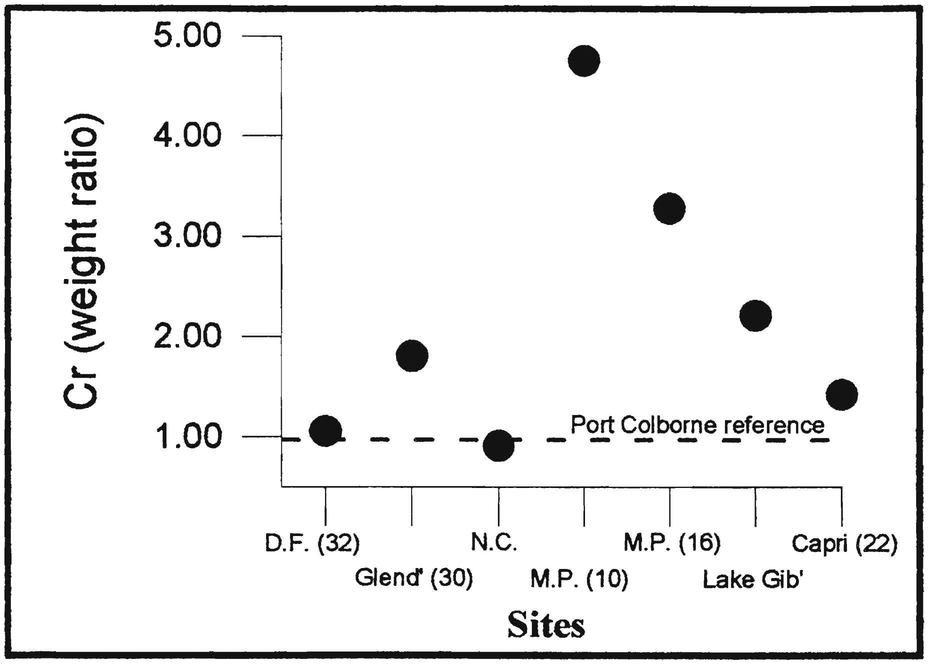


Figure 46: Cr dry weight ratios of zebra mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

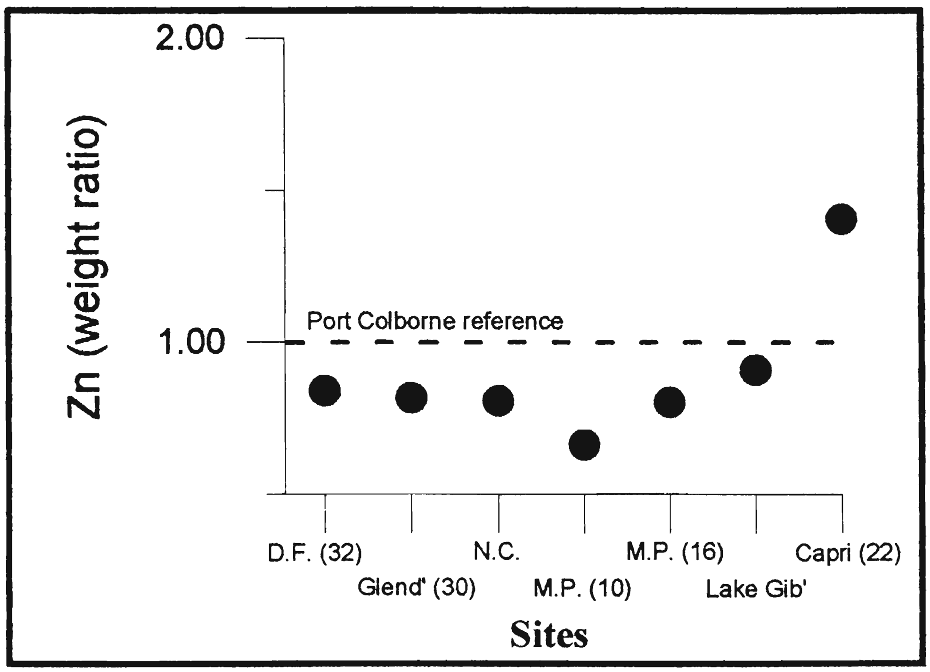


Figure 47: Zn dry weight ratios of zebra mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

Zn content in mussels at Capri (site 22) seemed to increase, whereas decreases were observed in the mussels at the other stations (Figure 47). Zebra mussels from Lake Gibson had the smallest decrease in Zn content, whereas site 10 (Martindale Pond) mussels had the greatest decrease relative to the Port Colborne reference samples.

Lead concentrations appear to have increased in mussels from all biomonitoring stations (Figure 48). In particular, Pb in mussels from Capri (site 22) increased by almost an order of magnitude relative to the Port Colborne reference concentration, while Lake Gibson zebra mussels had the lowest increase (2 times). Mussels from the remaining five stations had increases ranging from 2.9 to 3.5 times relative to the reference population.

A record was made every time a metal concentration observed in the mussels was at the two highest levels for all groups. Mussels from the Capri site fulfilled this criteria four times for Cu, Cd, Zn and Pb (Table 13). Site 16 was second, since zebra mussels had three high metal contents (Ni, Cr, and Pb). Only the mussels from the Niagara College site were low in metals not to be ranked in the chart. The two sites with seemingly the highest metal content increases relative to the Port Colborne reference tissues were noted for each monitoring site. A ranking of high elemental tissue contents follows in Table 13.

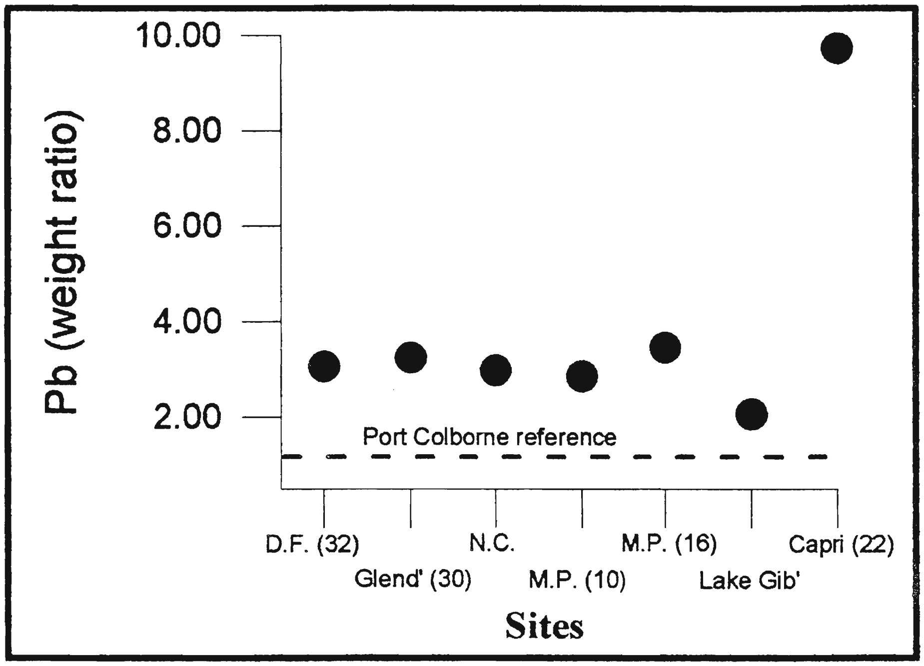


Figure 48: Pb dry weight ratios of zebra mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30),
N.C. = Niagara College, M.P. (10) = Martindale Pond (10),
M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

Table 13. Number of times each site contained the two highest zebra mussel-tissue metal contents.

Location	# of times in the top 2	Elements
Capri (22)	4	Cu(2), Cd(2), Zn(1), Pb(1)
Site 16	3	Ni(1), Cr(2), Pb(1)
Lake Gibson	2	Cu(1), Zn(1)
Decew	2	Cd(1), Al(2)
Glendale (30)	2	Ni(2), Al(1)
Site 10	1	Cr(1)

Quagga Mussels. The following discussion involves relative metal concentrations after 159 days and does not include the Capri site (22), since all quagga mussels had died during the second phase of the biomonitoring process. The metal content ratios are used to compare mussel tissue chemistry between locations relative to the Port Colborne reference values.

All specimens, except for one, had lower Cu contents after the 65 and 159 day experiments than the original specimens from Port Colborne (Figure 49). In most stations, the 159 day experiment mussels had greater Cu concentrations in comparison to their 65 day counterparts. Tissues sampled at 65 days had greatest concentrations in Capri (22) and Lake Gibson samples. After 159 days, Lake Gibson quagga mussels appear to have had greater Cu values than the reference Port Colborne mussels and the next highest values were noted in mussels from site 10 (Martindale Pond).

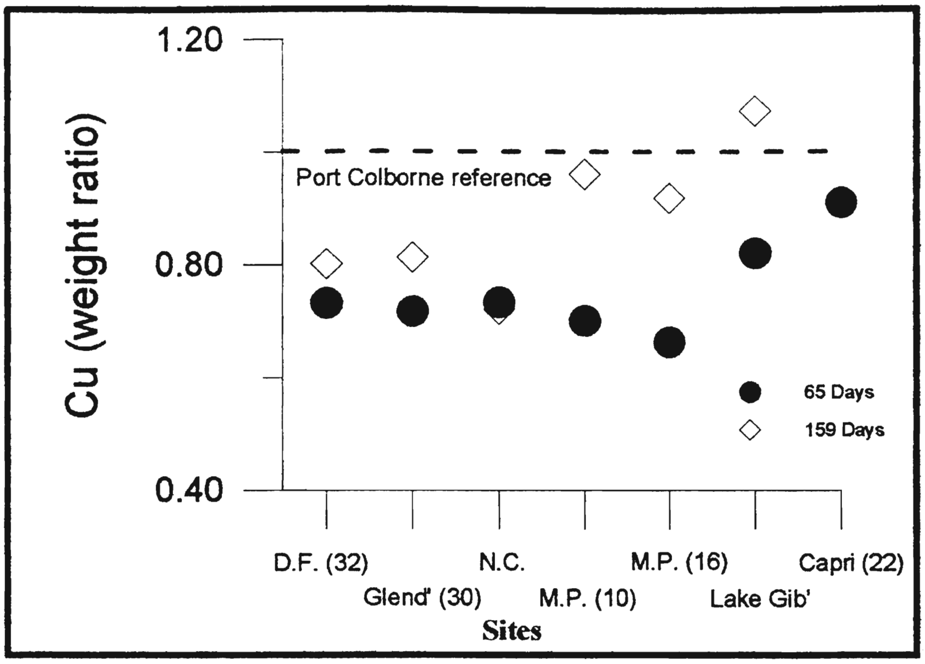


Figure 49: Cu dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

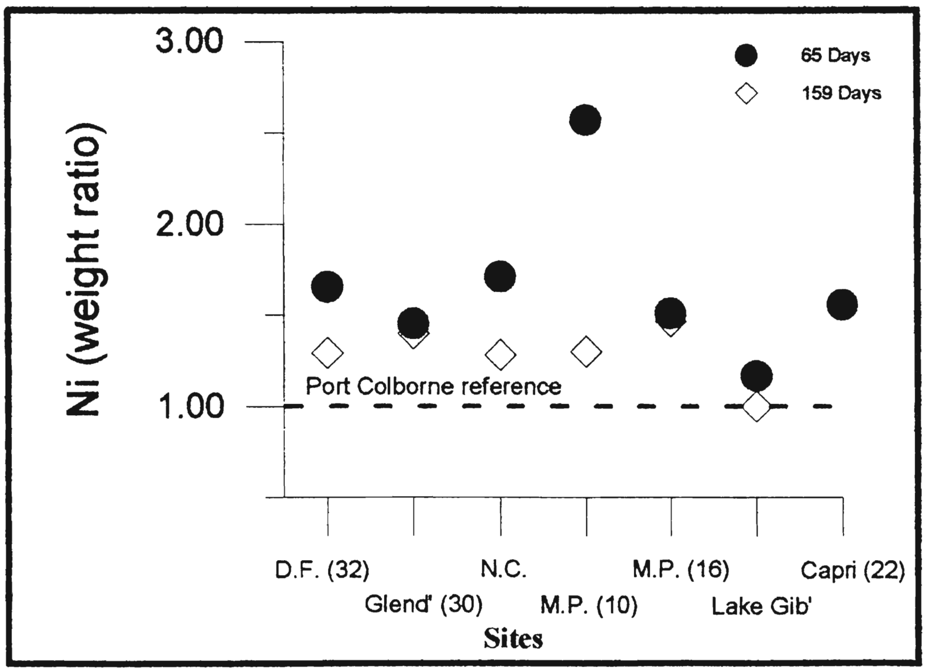


Figure 50: Ni dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

In general, all quagga mussel groups from each site seem to have Ni content increases relative to the Port Colborne reference tissue values. All stations after 159 days show a decrease in Ni concentrations relative to those observed in their 65 day couterparts (Figure 50). For the 65 day period, the highest concentrations were observed in mussels placed at site 10 (Martindale Pond) and Niagara College. During both periods of biomonitoring, the Lake Gibson mussels had Ni contents similar to those of the reference mussels. The greatest decrease between the 65 and 159 day periods appears to have occurred in the mussels from site 10. The least amount of change, during these periods, was observed in Glendale (30) and site 16 mussels. After 159 days of monitoring, the stations with the highest concentrations were found in mussels used at Glendale (30) and site 16 (Martindale Pond).

The majority of specimens from each site seem to have increases in Cd concentration relative to the Port Colborne reference samples. Lower Cd concentrations in mussels relative to reference values were observed at Niagara College after 65 days (see Figure 51). Other reductions occurred in mussels used at site 10 after 159 days and at site 16 during both time periods. Lake Gibson, Niagara College, Glendale (30) and Decew Falls mussels had increased Cd concentrations at 159 days relative to the 65 day experiment. The greatest increase occurred during the 65 day period at Capri (site 22). The next highest concentration was found in mussels from the Decew Falls station. The highest concentrations at 159 days were recorded in mussels from Lake Gibson followed by those from Niagara College.

All biomonitoring stations seem to have had increases in Al concentrations relative to reference values (Figure 52). The highest concentrations at the 65 day period were found in mussels used at site 16 and Glendale. The largest increase (> 28 times) was observed in

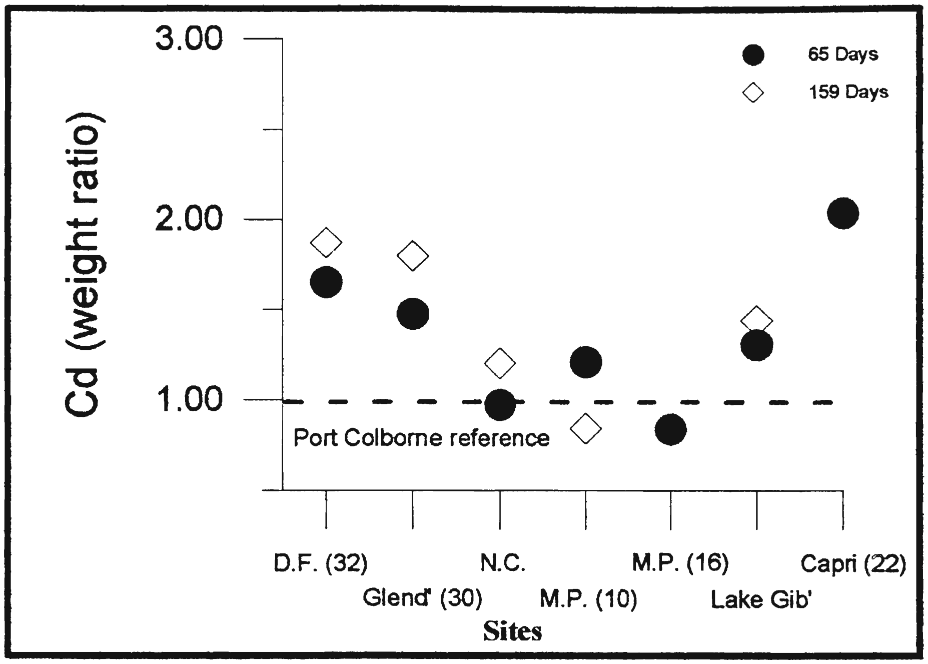


Figure 51: Cd dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

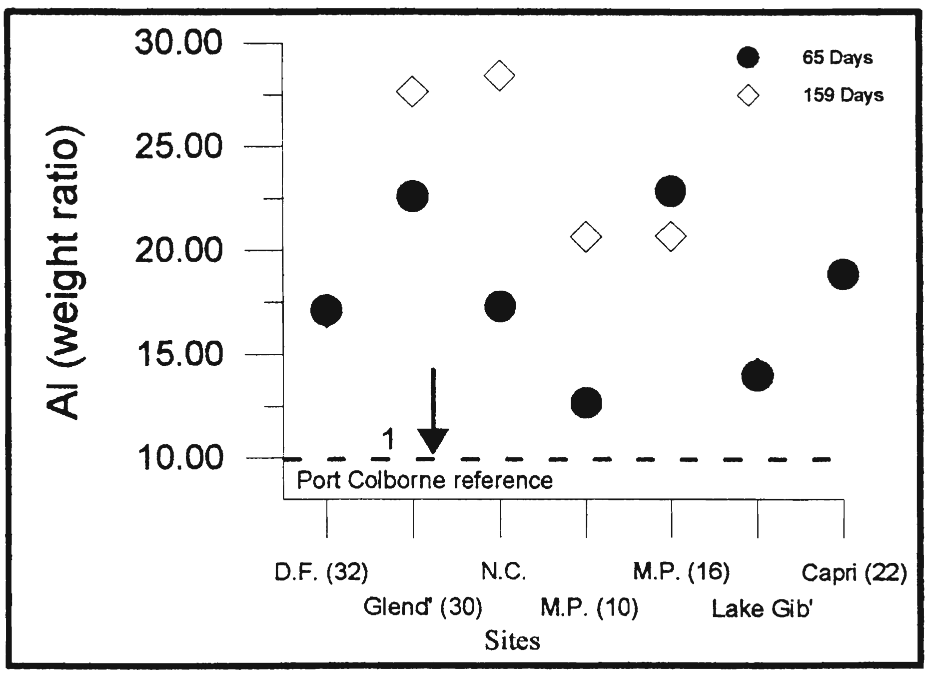


Figure 52: Al dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

mussels used at Niagara College (site 1) after 159 days. Tissue sample contents from Decew Falls and Lake Gibson were constant during the two time periods. This may suggest that 65 days is sufficient time for quagga mussels to equilibrate for at least Al. Glendale (30), Niagara College, and site 10 had large increases over the two survey periods.

All specimen groups for both time periods, except one (65 days), appear to have increases in Cr content relative to the reference tissue values. A high Cr anomaly was found after 65 days at site 10 (Figure 53), but after 159 days tissue contents were down to values similar to other stations. Lake Gibson mussels appeared to have the second highest concentrations after 65 days. After 159 days, highest Cr concentrations were found in mussels used at Lake Gibson and site 16. Cr values in mussels at Decew Falls and Lake Gibson appeared to be similar during both periods of monitoring, and is evidence that the mussels may have reached equilibrium during the 65 day experiment. Mussels from Glendale (site 30), Niagara College and site 16 showed increasing concentrations during the two time periods.

Only one group of quagga mussels, relative to the Port Colborne reference mussels, appears to have an increase in Zn content. Capri (site 22) mussels, after 65 days, were the only samples that exhibited increases in Zn concentrations relative to the reference specimens (see Figure 54). The second highest Zn concentrations were in mussels from Lake Gibson. Lake Gibson mussels had constant concentrations during both periods of biomonitoring. The other five stations had slight increases in Zn during the second time period. The highest concentrations after 159 days were in mussels used at Glendale (30) followed by those at Lake Gibson.

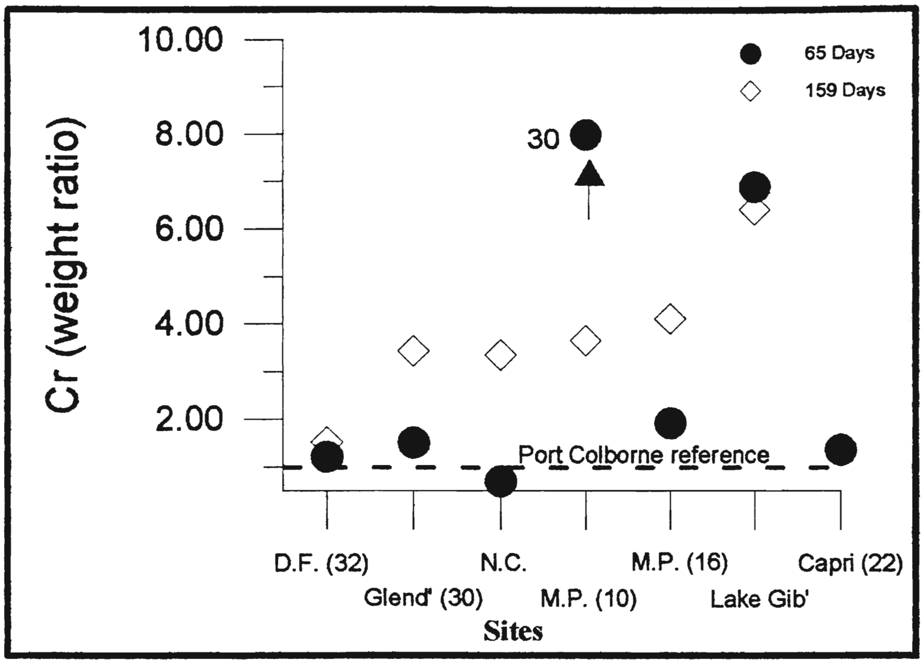


Figure 53: Cr dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30),
N.C. = Niagara College, M.P. (10) = Martindale Pond (10),
M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

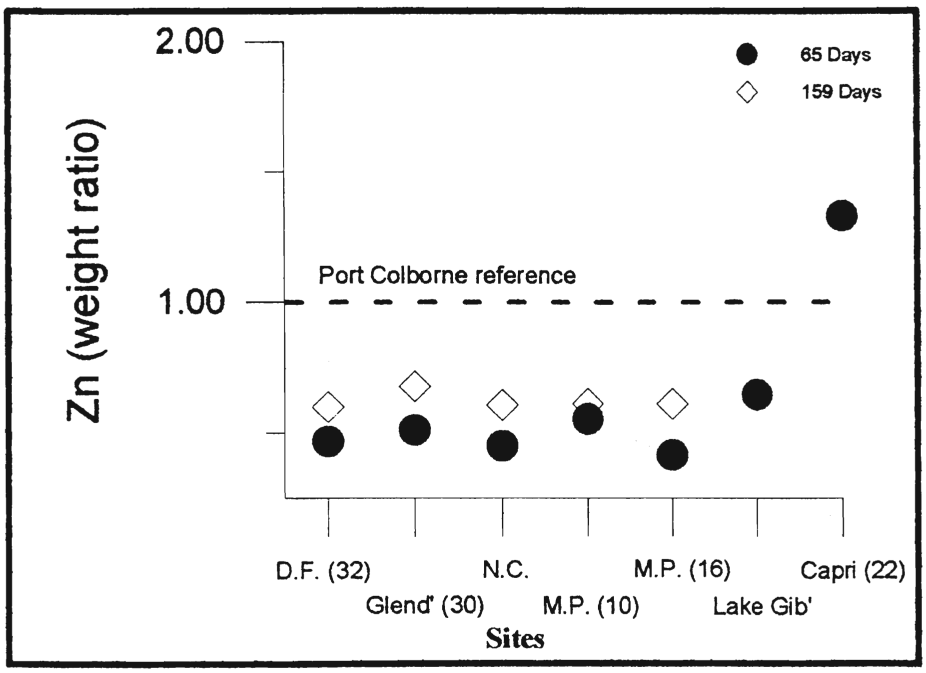


Figure 54: Zn dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30),
N.C. = Niagara College, M.P. (10) = Martindale Pond (10),
M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

All specimens, except for those from two localities (159 days), seemed to have higher Pb concentrations than the Port Colborne references. Capri (site 22) mussels had the highest Pb concentration (Figure 55) after the 65 day period; after 65 and before 159 days all specimens had died due to possible metal poisoning. The next highest concentration was found in mussels used at site 16 (Martindale Pond). Mussels from site 10 had greater Pb contents than the reference mussels, and were constant for the duration of the entire experiment. Niagara College, site 16, and Lake Gibson mussels had decreases in Pb contents during the second period. Site 16 and Lake Gibson mussels after 159 days had concentrations less than the reference values, while the mussels from Glendale (site 30) and Decew Falls both had the highest concentrations and increases during the second time period.

The two sites with the seemingly greatest metal content increases in quagga mussel tissues, relative to the Port Colborne references, were noted for each site during the two monitoring periods. The ranking of high metal contents follows in Table 14.

Table 14. Number of times each site contained the two highest metal contents in quagga mussel tissues, and their rank.

Location	Day 65	Metals	Day 159	Metals
Capri (22)	4	Cu(1), Cd(1), Zn(1), Pb(1)	N.A.[a]	N.A.[a]
Decew Falls	1	Cd(2)	2	Cd([b]), Pb(2)
Lake Gibson	3	Cu(2), Cr(2), Zn(2)	3	Cu(1), Cr(1), Zn([b])
Niagara College	2	Ni(2)	1	Al(1)
Site 16 (MP)	2	Al(1), Pb(2)	2	Ni([b]), Cr(2)
Site 10 (MP)	2	Ni(1), Cr(1)	1	Cu(2)
Glendale (30)	1	Al(2)	5	Ni([b]), Cd([b]), Al(2), Zn([b]), Pb(1)

Note: [a] All specimens had died before 159 day survey period was completed. [b] Concentrations are indistingushable.

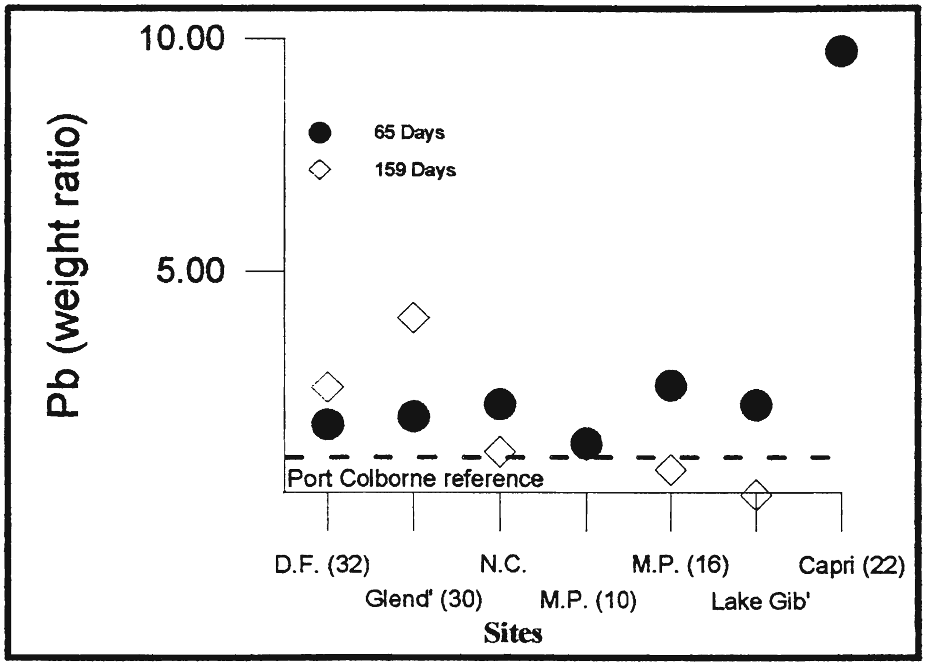


Figure 55: Pb dry weight ratios of quagga mussels from the various sites and Port Colborne reference.
Note: D.F (32) = Decew Falls, Glend' (30) = Glendale (30), N.C. = Niagara College, M.P. (10) = Martindale Pond (10), M.P. (16) = Martindale Pond (16), Lake Gib' = Lake Gibson,

DISCUSSION

Zebra and Quagga Mussels

Although quagga and zebra mussels belong to the same genus and share almost the same ecological niche, quagga mussels are better adapted to, and survive better in colder, and deeper waters (G. Mackie, pers. com. 1995). In addition, as shown in Chapter 2, the two species seem to incorporate metals at different rates and have different regulatory capacities, thus environmental stress (anthropogenic chemical pollution) may impose further differences in survival rates between the two species.

The paired Wilcoxian test data at the 95% confidence level suggests that there is no difference in mortality rates between the two species groups (quagga and zebra mussels at 65 days) since both groups had intervals which straddle zero (Table 11). However, at the 90% confidence level the zebra and quagga mussel groups do not straddle zero, which indicates that there is a significant difference between the two mussel death rates. There was no statistical difference between the species mortality rates, which may indicate that the data set was too small to differentiate between them or that environmental parameters were not exceeded for either mussel group. There was no statistical difference between the two quagga mussel group's (65 and 159 days) at the 95% and 90% mortality rates since both tests produced intervals about zero. This suggests that biological impacts on mortality rates were not observed (e.g., old age) in the population.

Chi^2 tests of the two populations (zebra and quagga mussels at 65 days, and quagga mussels at 65 days and 159 days) support differences in mortality since both had values greater than the 95% cutoff at 6 degrees of freedom, which suggests that there is a significant difference in death rate between localities. This implies that either an environmental (anthropogenic) stress or natural non-biological stress (unfavourable natural parameters) or a combination of both exist, within the watershed at specific sites.

Although the Chi^2 tests suggests that there are differences in site death rates, confidence interval testing of mortality means, at the 95% level, was not able to identify the anomalous site(s) (Figures 40 and 41). Although, the Decew Falls site is not statistically different from the other sites in the two population comparisons, it has higher mussel mortality rates than Lake Gibson, site 10 (Martindale Pond), and site 16 (Martindale Pond) counterparts. In addition, the Capri (22) quagga mussel population (65 days and 159 days), although not statistically different, appears to have a greater mortality rate than Lake Gibson, Glendale (30), Niagara College (1), site 10 (Martindale Pond), and site 16 (Martindale Pond) populations. Although, it can not be proven with the current data set, it appears that the high mortality rate at the Capri (22) site, which occured between 65 days and 159 days (from January to April), corresponding to the Spring period may be either related to road salt runoff (this is supported by the high salinity data obtained at site 22 (Water Quality, Chapter 1) during January) or it may be related to higher concentrations of toxic metals in the water due to increased exchange capacities of the sediments.

As mentioned in the introduction, active biomonitoring represents a short interval in water chemistry and comparisons between sediment chemistry and tissue bioaccumulation may be limited. However, similarities do exist between the biomonitors and sediment chemistry. Lake Gibson mussels had relatively high Cu concentrations. This supports the Cu loading conclusion derived from sediment testing, where total Cu content was found to be above the LEL (Persaud *et al.*, 1992). Mussels used at the Capri (22) site also had high Cu contents that were reflected in the total and exchangeable metal sediment fractions (Tables 3 and 4). Ni biomonitoring values were relatively high at Glendale (30) and Site 16. This supports the total sediment chemistry at Glendale which had values greater than the LEL. Similarly, sediments at site 16 had concentrations above SEL for total Ni content and above the upper limit for exchangeable Ni (Chapter 1).

High Cd concentrations were consistently found in both biomonitors for both survey periods at the Decew Falls and Capri sites. The Decew Falls sediments had total and exchangeable Cd concentrations below the lower limit. This core was taken on the other side of the creek and may not be representative of the biomonitoring test area. In contrast, upstream values at core site 33 in SHPP were above the LEL and upper limit for total and exchangeable Cd fractions. The Capri (22) sediments had the highest total and exchangeable fractions of Cd found anywhere in the study (Chapter 1). The mussels used in the biomonitoring experiments support the heavy metal loading which may be the result of discharge from the city storm sewer outfall at this locality.

Relatively high Al tissue concentrations found at the Decew Falls site are reflected in the sediment samples. Sediments at Decew Falls had total Al values greater than the LEL, and the exchangeable fraction was above the upper limit. As concluded in Chapter 1, high Al concentration is contributed to the Twelve Mile Creek by the 34C tributary in SHPP.

Lake Gibson and site 10 mussels bioaccumulated Cr. This was reflected in total sediment concentration being greater than the LEL at both sites. In contrast to the tissue samples, both sites had sediment exchangeable fractions below the lower limit (Chapter 2).

High Zn concentrations were consistently found in biomonitors used at Lake Gibson and Capri (22) sites. Similar to Cd, total sediment Zn concentrations were highest for the area near the city outfall at the Capri site (22) . Lake Gibson sediments also had Zn concentrations greater than the LEL at sites 37 and 38.

Biomonitors used at Glendale (30) and Capri (22) were consistently high in Pb. Total sediment Pb concentrations were below the MDL at Glendale (30). However, exchangeable fractions were above the upper limit. The Capri mussels had very high Pb accumulations during the first period. This supports the high sediment loadings, which had total Pb concentrations above the LEL and exchangeable Pb concentrations above the upper limit at the Capri site (22).

It is possible that high Pb, Zn, Cu and Cd concentrations in the water, during the second interval of the biomonitoring survey (65 days to 159 days), may have contributed to the total quagga mussel death at the Capri (22) station. In particular, bioavailable fractions of Pb and Cd were especially high after the 65 day testing period. Since the site was near a storm city outfall (S39; Figure 2), which is located beneath the QEW, it is likely that the increased death rate after the first testing period was induced by road salt run-off. A possible scenario is that the saline solution would sink and mix with the sediments, thereby inducing cation exchange and increasing the toxic capacity of the metal ions which became bioavailable. Equally possible, is that the road salt run-off was responsible for the mortality during the second interval.

The similarity of elemental ratios of specific metals (Al and Cr), calculated for both periods of biomonitoring, suggest that 65 days may be enough time for quagga mussels to reach equilibrium with the water.

Background values for zebra mussel are well established in the literature for Cd, Zn, Cu, Cr, and Pb (de Kock, 1993; Mersch, Pihan, 1993; Kraak and Toussaint, 1993; Karbe *et al.*, 1975). In addition, Secor *et al.* (1993) published comparable zebra mussel tissue data (Cd, Cr, Cu, Ni, Pb and Se) from the Niagara River. Lake Gibson mussels exceeded background level and Niagara River values for Cu. All sites, except site 10, had zebra mussel Ni values greater than Niagara River tissue values (Appendix 3). Translocated mussels from sites 10 and 16 had Cr values greater than background tissue and Niagara River zebra mussel tissue values. All sites had Pb tissue concentrations that were greater than background levels (Table 15). In addition, mussels from all sites, except for those from Lake Gibson, exceeded the Pb Niagara River mussel value.

Table 15. Background, Niagara River, and TMC watershed highest values (ppm) of metals in zebra mussels

		Cd	Cr	Cu	Mo	Ni	Pb	Se	Zn
Background									
de Kock (1993)		0.54		14.3					158
Mersch and Pihan (1993)		0-1	0-3.5	0-17			0-1.3		
Kraak (1993)		1.2		13.6					
Karbe (1975)		0.7	6.6						113
Niagara River									
Secor *et al.* (1993)	< 1.5 cm	5.03	5.04	11.0	2.38	18.9	3.41	2.7	160
	> 1.5 cm	5.89	4.14	9.54	0.97	20.3	3.23	6.8	168
Tweleve Mile Creek Watershed									
	2.5 - 3.0 cm	1.90[a]	7.09[b]	22.17[c]		34.54[d]	13.28[e]		171.91[e]

Note: [a] Decew Falls. [b] Site 10 (Martindale Pond). [c] Lake Gibson. [d] Glendale Avenue. [e] Capri (22).

SUMMARY

Collective biomonitoring results show that bioavailable Al appears to be elevated in the Twelve Mile Creek watershed and may be contributed by a SHPP tributary (core sediment in Table 3, Chapter 1). Capri (site 22), site 10 and Glendale seem to be sites where high metal (Cd, Pb, Cu, Zn, As) concentrations bioaccumulated. These sites are immediately downstream of city storm sewer outfalls, which may be possible point sources. Sediment evidence suggests that not all Capri (site 22) metal concentrations came from the storm sewer outfall (S39, Figure 2). The upstream combined sewer overflow discharge and industrial discharge upstream of site 22 probably contributed to the observed levels. Lake Gibson, a waterway associated with the Welland Canal system, had high bioaccumulative metal contents which most likely contributed to the high tissue values observed at the Decew Falls testing station. Although not statistically significant, SHPP, with the least anthropogenic sediment impact in the watershed (Tables 3 and 4, Chapter 1), had a 100% unionid survival rate. This was not observed at any of the other seven survey localities.

The highest Al contents were recorded in zebra mussels from Decew Falls and quagga mussels from Glendale (Tables 9 and 11). Thus, it may be beneficial to use a variety of filter feeders for biomonitoring studies. The quagga mussels appear to come to equilibrium within 65 days of translocation.

Zebra and quagga mussels after 65 days seem to have had large increases in Cd and Zn content, for both Lake Gibson and the Capri site. This may also suggest that these metals may in fact be at much greater total concentrations due to the competitive nature of organics (TPH, Chapter 1) which were high at these sites.

CONCLUSIONS

The active biomonitoring part of the study using zebra mussels, quagga mussels, *Anodonta* sp., and *Elliptio* sp, leads to the following conclusions.

1. Relative to Port Colborne Harbour (Port Colborne, Ontario), the Twelve Mile Creek watershed appears to be elevated in bioavailable Al.

2. There was no statistical difference in death rates between zebra and quagga mussels after 65 days of biomonitoring.

3. There is a difference in death rates between sites. Unfortunately, the data base did not allow us to differentiate between sites.

4. Storm sewer outfall S39 (site 22) is a possible contributor of bioavailable Cd, Zn, and Pb and may support the high sediment total and exchangeable Cd, Zn, and Pb values (Tables 3 and 4, Chapter 1). High salinity due to road salt run-off could have induced cation exchange of metals on clay surfaces from upstream sources and increased their availability. Since neither case can be statistically proven within the current data base, a combination of both processes is equally valid.

5. Quagga mussels appear to have reached equilibrium within 65 days of translocation.

6. Differences in metal accumulations between bivalves suggest that biomonitoring screening studies must include a variety of different organisms.

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APPENDIX 1

SEDIMENT DATA AND CORE LOGS

Total Metal Analysis
All values are ppm

		Ni	Cu	Al	Cr	Cd	Pb	Zn	As	Se
			Guidelines (Persaud, 1992)							
Sediments LEL		16	16		26	0.6	31	120	6	
Sediments *SEL		75	110		110	10	250	820	33	
	depth cm									
opt1-1	0-4	41.37	34.00	49895.31	6.15	0.7708	18.24	124.62	13.67	1.92
opt1-2	4-6	38.45	30.93	47851.20	45.95	0.7274	18.67	115.83	13.21	0.59
opt1-3	11-12.5	34.04	30.31	47538.64	20.27	0.5589	14.94	111.51	10.86	2.22
opt1-4	17.5-19	38.78	30.94	47502.56	40.16	0.6672	15.95	101.78	12.17	2.34
opt1-5	24-25	51.04	39.29	46017.61	42.69	0.7664	15.63	117.81	11.75	2.49
opt1-6	28.5-29.5	36.78	41.78	47611.85	43.50	0.4535	18.29	115.42	9.64	1.69
opt1-7dup	33-34	39.34	39.21	48328.25	41.47	0.2544	18.40	109.72	7.45	0.60
2-1	0-2	37.70	32.46	54881.62	56.57	0.5947	24.29	126.12	17.25	2.20
2-3	24-26	43.03	43.27	53948.73	55.72	0.4970	24.77	132.53	5.02	1.40
2-4	33-34	53.98	38.89	55085.84	61.75	0.4140	26.83	280.40	8.72	2.48
2-5	39-40	70.23	44.57	54171.98	63.10	1.3883	28.36	254.63	8.80	1.80
2-6	54.6-56	*128.38	51.91	45669.35	55.70	1.4939	33.14	173.48	3.73	0.05
2-7	64-66.5	*96.09	39.12	36832.53	43.28	0.9742	34.13	133.40	10.76	2.21
2-8	72-73	42.67	34.08	74328.87	78.29	0.0212	*269.03	140.39	*49.54	1.78
2-9	80-82	42.79	35.78	29369.93	75.62	0.1128	*984.16	214.85	8.62	4.61
5-1	0-2	30.43	23.54	37654.71	34.63	2.0516	16.65	107.41	9.43	1.61
5-2	4-5	32.16	20.93	35928.39	31.92	0.3633	16.38	95.44	7.12	2.33
5-3	7-8	37.96	20.12	35398.90	34.42	0.3053	16.95	112.21	7.46	3.82
5-4	9-10	50.15	31.45	45065.99	45.19	0.9177	22.15	205.02	4.27	1.69
5-5	10.5-11.5	32.96	23.57	44865.90	36.76	0.5058	16.24	80.68	15.06	0.96
5-6	26-28	*119.63	44.11	43548.27	40.14	0.8792	34.19	146.82	7.60	0.68
5-7	46-47	*132.15	50.72	44072.95	42.15	1.0593	35.68	165.22	2.28	0.19
5-8	70-71	*117.99	42.61	39873.48	42.47	0.7761	28.97	117.47	19.90	2.21
5-9	75-76	*106.35	40.23	43541.70	41.79	0.7133	26.98	113.18	*62.57	0.11
5-10	79-81	36.90	20.72	39809.49	26.38	0.1751	15.90	60.13	*52.47	1.69
1day-1	0-2	48.59	30.49	44872.51	45.79	0.8128	23.18	213.65	6.46	2.95
1day-2	8.5-10	59.33	33.39	48661.83	47.13	0.7518	28.41	251.24	10.41	3.89
1day-3	16-17.5	46.09	31.46	42698.19	41.00	0.6419	25.60	232.06	8.53	5.45
1day-4	23-25	66.09	46.73	47274.73	77.96	1.1643	38.40	159.88	4.26	4.81
1day-5	39-41	62.59	42.13	49501.22	55.90	1.4030	35.34	137.72	*62.97	2.82
1day-6	51-52	*85.66	45.79	47681.05	56.57	0.8897	33.49	136.23	8.75	4.15
1day-7	51-52	*82.76	50.49	43878.15	53.06	1.3545	42.70	161.81	10.88	2.22
1day-8	57-58	*89.56	35.77	38292.43	39.90	0.5002	28.84	118.22	7.92	0.87
7-1	61-62	45.27	37.18	47955.88	53.89	1.8959	23.87	133.77	9.60	0.60
7-2	0-2	45.67	1.46	1890.83	1.86	0.0292	1.08	5.60	0.38	0.05
7-3	13-15	*98.02	36.88	39764.00	51.19	0.5263	41.99	108.50	9.35	3.29
7-4	22-25	51.29	1.06	1087.12	1.32	0.0289	0.90	3.10	0.20	0.09
7-5	26-27	*84.01	32.38	35652.56	42.75	0.6543	32.44	95.06	5.25	3.70
7-6	32-33.5	51.09	28.92	40140.51	47.94	0.3245	31.19	103.48	4.86	4.36
7-7	41-42.5	38.71	25.82	41632.23	31.29	0.1121	18.64	56.79	4.06	4.80
4-1	0-3	63.16	32.32	56846.67	53.82	0.8489	21.56	133.26	7.15	4.09
4-2	3-5	37.71	31.62	59403.18	52.05	0.7425	20.00	127.51	5.37	3.90
4-3	17-18	59.19	32.33	58002.30	50.07	0.4808	26.47	175.34	4.46	3.88
4-4	23-24	*76.05	36.47	60571.75	53.84	0.7887	23.45	132.82	4.21	2.43
4-5	31-32	56.12	32.26	60410.11	53.04	0.4749	23.21	121.51	3.75	3.83
4-6	46.5-48	35.99	26.36	60901.88	50.95	0.2462	23.79	89.75	2.74	2.40
4-7	61-63	35.76	25.14	63090.01	56.32	0.1131	25.14	97.54	2.27	4.69
4-8	72-73	36.50	25.13	68005.14	64.91	0.0446	28.92	100.31	2.49	4.58
4-9	78-79	42.36	20.79	61067.67	47.26	0.0637	17.33	76.71	4.92	4.84
4-10	83-85	35.45	22.11	63939.26	51.76	0.2567	19.64	80.86	16.81	3.81
4-11	98-100	38.44	26.37	75434.33	61.32	0.2914	18.45	153.27	18.91	9.33
4-12dup	108-110	34.41	23.00	63922.05	47.24	0.2527	14.24	119.60	18.44	4.68

		Ni	Cu	Al	Cr	Cd	Pb	Zn	As	Se
Sediments:	LEL	16	16		26	0.6	31	120	6	
Sediments:	*SEL	75	110		110	10	250	820	33	
6-1	0-2	63.03	54.73	43177.68	49.31	2.5842	31.79	124.98	5.41	0.77
6-2	9-11	*148.90	100.67	46054.04	69.94	3.0605	93.97	228.45	8.04	1.64
6-3	25-26	*175.37	104.65	46926.68	63.95	1.5294	89.14	207.56	5.12	1.07
6-4	35-36	*90.93	58.22	41378.06	46.80	0.8900	40.34	139.24	4.03	1.60
6-5	43-45	*83.17	46.78	43576.05	45.14	0.9647	30.47	138.30	6.77	<0.00743
6-6	63-65	35.74	25.33	46792.49	49.70	<0.0069	44.92	96.97	3.86	0.90
6-7	66-67	22.32	24.72	44154.71	39.66	<0.0069	26.84	82.86	3.52	0.17
6-8	73.5-75	*97.14	97.05	47993.33	57.83	0.9690	119.12	213.65	9.25	0.45
6-9	78-80	47.73	39.80	50403.07	51.68	1.4443	38.99	85.88	6.46	0.57
6-10dup	87-89	68.67	71.27	52181.01	54.11	2.6256	86.64	158.68	9.08	1.42
c1	0-2	33.46	22.56	42674.41	33.89	0.6904	23.19	44.00	7.42	<0.00464
c2	2-6	39.03	36.44	47526.18	53.60	0.7894	34.11	70.05	5.89	0.23
c3	6.5-11.5	*103.77	47.42	52297.56	57.05	1.5114	44.59	85.25	10.71	0.58
c4	11.5-14	36.25	24.61	45966.06	39.62	0.2867	17.57	44.68	7.37	0.02
c5	14-16	36.74	25.74	52197.01	48.04	0.5142	17.93	52.89	9.53	0.75
c6	16-24	31.79	26.07	56660.30	50.41	0.1041	18.88	56.68	7.72	0.94
c7	24-31.5	33.89	23.99	54532.52	48.55	0.6119	16.62	54.90	4.26	0.29
b1	0-3	33.23	53.59	47313.34	46.67	0.9395	64.96	100.66	2.12	1.41
b2	3-8	31.68	50.59	45365.44	53.01	0.8497	80.32	89.67	3.81	1.18
b3	8-13.5	31.03	48.26	45747.51	52.83	1.2213	73.42	81.87	2.48	0.48
b4	13.5-19.5	29.79	37.28	54751.47	52.80	0.7675	62.83	95.87	6.19	0.90
b5	19.5-24.5	30.28	34.68	54209.72	55.32	1.1083	61.03	84.30	3.98	1.13
b6	24.5-30.5	30.13	38.08	53841.69	59.70	1.0104	78.18	96.32	6.96	1.08
b7	30.5-31.5	33.74	29.37	48196.39	58.30	0.7810	50.89	60.41	8.50	1.70
a1	0-2	33.12	28.92	34856.23	39.41	0.6599	21.64	63.53	0.68	<0.00345
a2	2-8	*78.76	57.91	43577.27	56.50	1.4656	58.23	112.79	5.66	<0.00345
a3	8-16	*88.52	45.31	32483.07	50.65	0.8870	42.63	80.89	5.11	0.23
a4	16-25.5	46.48	37.24	32839.71	40.72	1.0311	28.94	57.86	0.46	0.16
a5	25.5-28	34.00	40.55	54968.78	56.96	0.4259	42.42	74.71	5.28	0.78
a6	28-31.5	36.13	27.89	57514.01	61.34	0.1023	50.38	63.19	3.96	0.73
ptCol hbr	0-2	*141.70	56.35	30247.10	47.34	1.2081	61.83	138.21	0.46	0.03
JohnstHbr	0-2	21.87	15.54	21856.79	34.70	0.3947	31.42	47.20	1.15	<0.00345
stClr1	0-4	28.52	5.45	26991.74	22.68	<0.0096	11.27	24.51	1.04	<0.00345
stClr2	4-8	29.72	18.60	36102.90	60.46	0.2051	143.07	68.47	5.73	0.14
stClr3	8-16	41.51	26.38	34438.52	51.59	0.5115	22.26	64.25	3.37	0.78
stClr4	16-22	35.66	24.13	36959.74	64.02	0.3267	21.47	61.69	0.89	0.56
stClr5	22-26	73.28	21.07	34726.25	67.19	0.2453	19.19	63.59	2.16	1.10
25-1	0-6.5	44.19	41.10	62612.65	79.14	0.9297	23.16	27.04	8.59	<0.00743
25-2	6.5-10.5	*154.49	*188.72	44390.15	*147.23	0.4607	-0.08	141.99	9.81	<0.00743
27-2	3-5.5	34.83	*166.84	51762.50	86.55	0.5017	92.43	238.75	11.19	<0.00743
27-3	5.5-14	48.57	*456.74	49812.17	105.50	0.4702	217.05	305.25	8.19	<0.00743
27-4	14-17	41.10	*429.55	39765.22	88.59	<0.0096	132.02	165.93	9.72	<0.00743
28-1	0-6	34.13	27.14	50599.65	56.24	<0.0096	19.62	91.63	9.15	<0.00743
28-2	6-15	41.99	33.08	49206.97	69.52	<0.0096	15.01	83.48	29.26	<0.00743
28-3	15-19.5	35.59	33.90	51691.43	69.54	0.9655	29.73	112.77	3.89	0.08
29-1	0-5.5	38.81	25.82	62359.03	75.70	<0.0096	9.48	71.29	5.94	0.02
30-1	0-3	42.00	26.95	47071.67	56.37	<0.0096	9.65	73.29	2.81	0.05
30-2	3-10	31.43	27.71	48777.16	61.61	<0.0096	5.85	66.35	9.24	0.04
30-3	15.5-18	35.51	25.58	43990.34	62.73	0.8786	7.89	77.21	3.51	<0.0042
30-4	18-26.5	28.76	26.47	43839.29	55.66	<0.0096	5.47	66.28	4.53	0.04
30-5	30-31.5	54.91	25.36	41114.70	61.25	0.0589	12.40	67.63	4.32	0.04
31-1	0-3	29.46	21.92	41782.78	55.05	0.0744	12.46	70.58	3.96	<0.0042
31-2	3-10	28.61	23.23	43377.30	60.10	0.6627	9.40	72.44	4.66	0.18
31-3	10-20	26.96	25.85	41971.53	56.97	0.0655	9.66	64.94	3.93	<0.0042
31-4	25-30.5	23.04	19.62	32069.31	59.84	<0.0096	11.38	64.67	3.96	<0.0042
32-1	0-7	27.80	27.32	47082.34	59.50	<0.0096	7.85	69.02	3.76	0.22
32-2	10-15	26.91	25.11	41434.96	57.73	<0.0096	6.58	58.09	6.03	<0.0042
32-3	15-21	25.89	27.79	62382.93	59.41	<0.0096	6.72	104.13	6.17	<0.0042
32-4	21-26.5	27.83	25.75	45324.81	54.61	0.3078	7.87	54.04	3.35	<0.0042

		Ni	Cu	Al	Cr	Cd	Pb	Zn	As	Se
Sediments	*LEL*	16	16		26	0.6	31	120	6	
Sediments	*SEL*	75	110		110	10	250	820	33	
33b-1	0-5	27.94	23.87	36147.29	55.93	1.2647	14.46	85.11	3.40	N.D.
33b-2	5-13.5	35.94	26.05	44500.43	96.69	0.5755,	16.15	62.64	5.86	N.D.
33b-3	13.5-19	29.91	22.47	34130.51	57.14	<0.0096	14.45	71.11	2.28	N.D.
33b-4	26-29	62.43	22.87	31480.94	60.75	0.8867	9.34	70.30	2.64	N.D.
34a-1	0-5	28.78	23.89	35877.04	54.46	0.6220	13.39	61.62	2.56	<0.00301
34a-2	12-17	40.10	26.71	35412.86	64.50	<0.0096	14.73	78.74	3.52	0.10
34a-3	17-22	24.78	26.12	41543.14	58.05	0.1776	8.47	53.74	2.01	0.07
34a-4	27-31.5	26.73	24.99	39653.30	57.45	<0.0096	8.64	59.32	2.47	0.04
34b-1	0-8	25.75	22.33	35871.97	54.98	<0.0096	10.96	74.40	1.94	0.32
34b-2	8-16	63.93	25.26	33618.31	59.67	0.0724	13.06	81.09	3.06	0.13
34c-1	0-3	34.86	22.14	55904.66	61.44	0.3129	15.57	63.02	11.96	N.D.
34c-2dup	3-11.5	35.44	20.75	53880.09	60.24	0.1673	12.03	61.63	15.51	N.D.
34c-3	11.5-20	41.38	20.76	55618.21	60.10	<0.0096	11.65	66.41	14.63	N.D. .
34c-4	20-31	29.16	24.32	49611.25	52.34	0.0395	9.11	56.71	13.49	N.D.
35a-1	0-5	24.44	16.31	47606.40	53.93	0.0325	9.80	59.05	14.82	N.D.
35a-2	5-9.5	31.94	24.95	49287.13	56.03	0.7699	12.19	67.29	28.37	N.D.
35-a3	9.5-12.5	31.18	21.44	43113.86	42.91	<0.0096	13.10	79.48	23.54	N.D.
21-1	0-5	21.36	16.16	12791.93	21.20	<0.0096	20.20	31.15	3.48	N.D.
21-2	5-12	42.06	40.40	54092.94	84.52	<0.0096	76.00	82.80	*39.63	N.D.
21-3	12-20.5	35.34	31.17	49401.73	74.36	<0.0096	60.16	45.01	17.16	N.D.
21-4	20.5-26	32.74	27.38	45528.38	58.20	<0.0096	47.19	28.30	*49.37	N.D.
21-5	26-30.5	32.83	27.38	47928.76	62.61	<0.0096	45.99	34.24	13.80	N.D.
22-1	0-1.5	*82.87	54.55	37853.54	67.63	0.9747	51.50	70.49	9.82	N.D.
22-2	6.5-9	*91.79	94.66	40506.41	95.31	6.4363	64.76	131.00	11.87	N.D.
22-3	15-20	*98.01	69.13	38918.04	84.12	2.5418	80.56	149.54	5.21	N.D.
22-4	20-22	*101.18	68.89	41072.78	85.02	2.1830	71.11	165.44	*47.84	N.D.
23-1	0-9	48.53	75.58	35449.24	*153.65	0.7798	63.27	234.46	16.00	N.D.
23-2	9-11.5	56.56	80.05	41511.35	*158.21	0.8794	74.93	232.35	<0.005	N.D.
23-3	12-17	49.47	47.90	48131.77	102.44	<0.0096	33.76	110.42	4.17	N.D.
23-4	17-24.5	54.77	60.84	48304.36	*120.93	0.1294	36.36	119.86	5.51	N.D.
23-5	24.5-30	51.42	48.51	51631.29	89.36	<0.0096	28.21	107.51	5.97	N.D.
24-1	0-4	41.37	33.55	40563.43	65.94	<0.0096	22.88	108.17	3.46	N.D.
24-2	4-10	42.33	31.56	39069.25	61.11	<0.0096	21.20	106.46	7.46	N.D.
24-3	10-15	47.45	33.00	35309.55	55.75	0.2544	20.73	118.45	4.59	N.D.
24-4	15-23	35.61	27.35	37495.36	59.26	0.0330	21.95	92.99	6.24	N.D.
24-5	23-29	40.35	29.44	36881.31	60.60	0.0315	22.82	98.10	3.90	N.D.
26-1	0-4	44.01	32.90	51714.94	72.95	<0.0067	23.56	92.86	4.19	N.D.
26-2	10-14	43.39	33.83	54841.69	72.39	<0.0067	26.09	110.38	15.65	N.D.
26-3	17-20	44.23	45.56	49609.24	68.44	<0.0067	16.94	89.04	7.47	N.D.
26-4	20-24	44.81	33.86	60427.75	71.73	<0.0067	18.86	113.74	6.59	N.D.
26-5	24-25	58.87	239.56	46515.18	77.15	0.6033	70.05	211.07	33.63	N.D.
37-1	0-3.5	56.05	37.70	45856.71	67.79	<0.0067	49.84	120.87	15.29	N.D.
37-2	8-10.5	30.82	19.94	45994.31	54.41	<0.0067	21.82	67.23	6.44	N.D.
37-3	10.5-19	48.95	29.49	46986.56	63.82	0.1595	29.81	105.74	9.65	N.D.
38-1	0-4	56.18	49.79	46330.36	76.98	<0.0067	41.97	113.15	12.07	N.D.
38-2	8.5-11	40.12	29.49	58020.16	72.26	<0.0067	24.39	127.91	9.78	N.D.
38-3	11-17	31.09	22.36	38552.83	53.01	0.1191	22.76	74.86	8.18	N.D.
39-1	0-6	67.95	*125.93	38354.61	72.79	0.4544	153.51	404.61	17.98	<0.00352
39-2	6-14	*631.34	*4267.60	38499.21	*1161.39	*13.76	*4275.03	*10971.69	*83.01	<0.00352
39-3	15-20.5	51.03	87.39	25049.70	48.10	0.5998	122.64	178.61	6.57	<0.00352
39-4	20.5-29	51.40	99.46	37984.95	63.05	2.3789	103.79	255.33	6.18	<0.00352
39-5	29-31.5	*116.68	*140.23	47673.58	109.60	1.5412	*267.059	N.D.	N.D.	14.09
%Error		4.14	1.57	2.46	1.85	10.46	3.47	5.58	12.73	25.30
%Recovery		104.13	80.15	82.11	95.09	78.03	92.42	97.44	95.29	103.27

Available Fraction (ppm)

* Note ALL Fractions >MDL are Above the Upper Limits (CCME, 1991).

		Pb	Cr	Cu	Cd	Al	Ni
Lower Limit		0.001	0.002	0.002	0.0002	0.005	0.025
Upper Limit		0.007	0.02	0.004	0.0018	0.1	0.15
	Depth cm						
opt 1-1	0-4	<0.003	<0.006	0.525	0.2552	<0.08	<0.026
opt1-2	4-6	0.200	<0.006	0.589	0.1055	<0.08	<0.026
opt1-3	11-12.5	<0.003	<0.006	0.370	0.0573	1.80	<0.026
opt1-4	17.5-19	<0.003	<0.006	0.472	0.0666	1.62	<0.026
opt1-5	24-25	<0.003	<0.006	0.488	0.0651	0.41	<0.026
opt1-6	28.5-29.5	<0.003	<0.006	0.443	0.1215	1.37	<0.026
opt1-7	33-34	<0.003	<0.006	0.525	0.1371	1.79	<0.026
2-1	0-2	<0.003	<0.006	0.486	0.0773	4.99	<0.026
2-3	24-26	<0.003	<0.006	0.449	0.1373	<0.08	<0.026
2-4	33-34	<0.003	<0.006	0.784	0.1558	0.51	0.71
2-6	54.5-56	<0.003	<0.006	1.268	0.9172	0.14	4.17
2-7	64-66.5	<0.003	<0.006	0.828	0.6294	0.43	4.00
2-8	72-73	<0.003	<0.006	0.300	<0.0017	0.59	<0.026
2-9	80-82	1.307	<0.006	0.367	<0.0017	0.67	<0.026
5-3	7-8	<0.003	<0.006	0.436	<0.0017	<0.08	<0.026
5-4	9-10	<0.003	<0.006	0.266	0.1201	1.97	1.30
5-5	10.5-11.5	<0.003	<0.006	0.601	0.1988	1.18	0.23
5-6	26-28	0.293	<0.006	1.326	0.5760	<0.08	4.75
5-7	46-47	<0.003	<0.006	0.931	1.0215	<0.08	16.31
5-8	70-71	0.152	<0.006	0.453	0.6134	<0.08	5.79
5-9	75-76	<0.003	<0.006	0.288	0.5189	<0.08	6.26
5-10	79-81	<0.003	<0.006	0.091	0.0842	<0.08	1.95
6-1	0-2	<0.003	<0.006	0.209	0.6414	<0.08	0.79
6-3	25-26	<0.003	<0.006	0.496	0.6918	<0.08	9.82
6-4	35-36	<0.003	<0.006	0.307	0.4576	<0.08	5.87
6-5	43-45	0.433	<0.006	0.495	0.5460	0.04	4.66
6-6	63-65	0.363	<0.006	0.060	0.0000	0.13	<0.026
6-7	66-67	0.103	<0.006	0.086	0.0000	<0.08	<0.026
6-8	73.5-75	1.312	<0.006	1.158	0.9582	0.24	6.32
6-9	78-80	0.331	<0.006	0.292	0.3569	1.22	0.39
6-10	87-89	0.372	<0.006	0.279	0.7617	1.35	1.77
4-1	0-3	<0.003	<0.006	0.304	0.1325	<0.08	<0.026
4-2	3-5	0.358	<0.006	0.313	0.0860	<0.08	<0.026
4-3	17-18	0.310	<0.006	0.244	0.1429	0.23	<0.026
4-4	23-24	0.239	<0.006	0.435	0.4862	1.07	0.14
4-5	31-35	<0.003	<0.006	0.513	0.2266	<0.08	0.48
4-6	46.5-48	<0.003	<0.006	0.182	0.0753	<0.08	0.33
4-7	61-63	<0.003	<0.006	0.130	0.0556	<0.08	<0.026
4-8	72-73	<0.003	<0.006	0.102	0.0706	<0.08	<0.026
4-9	78-79	<0.003	<0.006	0.000	<0.0017	<0.08	<0.026
4-10	83-85	<0.003	<0.006	0.000	0.0164	<0.08	<0.026
4-11	98-100	<0.003	<0.006	0.161	0.0296	<0.08	<0.026
4-12	108-110	<0.003	<0.006	0.134	0.0171	<0.08	<0.026
7-1	0-2	0.162	<0.006	0.152	0.2186	<0.08	<0.026
7-2	2-4	<0.003	<0.006	0.165	0.0331	<0.08	<0.026
7-3	13-15	0.197	0.090	0.271	0.2216	<0.08	1.67
7-4	22-25	<0.003	0.042	0.396	0.4394	<0.08	2.85
7-5	26-27	0.084	0.051	0.135	0.0752	<0.08	2.75
7-6	32-33.5	<0.003	<0.006	0.020	<0.0017	<0.08	0.36
7-7	41-42.5	<0.003	<0.006	0.059	<0.0017	<0.08	0.82
1day-1	0-2	<0.003	<0.006	0.090	<0.0017	<0.08	0.30
1day-2	8.5-10	<0.003	<0.006	0.026	<0.0017	<0.08	0.85
1day-3	16-17.5	<0.003	<0.006	0.068	<0.0017	0.83	1.38
1day-4	23-25	0.311	<0.006	0.406	0.7391	2.03	2.99
1day-5	39-41	0.110	<0.006	0.370	0.8939	1.95	2.76
1day-6	51-52	0.217	<0.006	0.591	0.7318	2.49	2.02
1day-7	57-58	0.191985	<0.006	0.759215	0.858698	2.050753	2.373638
1day-8	61-62	<0.003	<0.006	<0.007	0.022295	0.300119	<0.026

		Pb	Cr	Cu	Cd	Al	Ni
Lower Limit		0.001	0.002	0.002	0.0002	0.005	0.025
Upper Limit		0.007	0.02	0.004	0.0018	0.1	0.15
c1	0-2	<0.003	<0.006	<0.007	0.327495	<0.08	2.482071
c2	2-6	<0.003	<0.006	<0.007	0.095707	<0.08	0.586882
c3	6.5-11.5	<0.003	<0.006	<0.007	0.24708	<0.08	7.265654
c4	11.5-14	<0.003	<0.006	<0.007	0.400994	<0.08	3.089668
c5	14-16	<0.003	<0.006	<0.007	<0.0017	<0.08	0.189543
c6	16-24	<0.003	<0.006	<0.007	<0.0017	0.237492	<0.026
c7	24-31.5	0.184275	<0.006	0.717704	0.017458	<0.08	<0.026
b1	0-3	0.062968	<0.006	0.440776	0.011694	<0.08	<0.026
b2	3-8	<0.003	<0.006	0.200837	0.055028	<0.08	<0.026
b3	8-13.5	0.135574	<0.006	0.222729	0.067787	<0.08	<0.026
b4	13.5-19.5	0.099853	<0.006	0.189721	0.043935	<0.08	<0.026
b5	19.5-24.5	<0.003	<0.006	0.197077	0.059123	0.61	<0.026
b6	24.5-30.5	0.123776	<0.006	0.206293	0.07344	0.866433	<0.026
b7	30.5-31.5	0.190582	<0.006	0.190582	0.019058	<0.08	<0.026
a1	0-2	<0.003	<0.006	0.229725	0.059728	1.110337	<0.026
a2	2-8	0.309662	0.040745	0.228172	0.537019	<0.08	0.888241
a3	8-16	0.12838	0.013263	0.283275	0.373269	<0.08	1.166345
a4	16-25.5	<0.003	<0.006	0.295124	0.482037	<0.08	1.04635
a5	25.5-28	<0.003	0.00828	0.190439	0.072863	<0.08	<0.026
a6	28-31.5	<0.003	<0.006	0.134832	0.037079	1.643262	<0.026
21-1	0-5	0.293853	0.123229	0.369686	0.462581	<0.08	<0.026
21-3	12-20.5	0.201279	0.05032	0.15096	0.010903	0.209666	<0.026
21-5	26-30.5	<0.003	0.046035	0.064449	0.007366	<0.08	<0.026
22-1	0-1.5	0.221854	0.062119	0.42596	2.283324	<0.08	2.129801
22-3	15-20	0.451093	<0.006	0.554469	1.059129	0.234944	2.396433
22-4	20-22	<0.003	<0.006	0.450484	0.813573	<0.08	3.036259
23-1	0-9	<0.003	<0.006	0.481038	0.195951	<0.08	<0.026
23-3	12-17	0.061105	<0.006	0.052376	0.111735	<0.08	<0.026
23-4	17-24.5	0.120138	<0.006	0.094394	0.128719	0.986848	<0.026
24-3	10-15	<0.003	<0.006	0.126545	0.047244	<0.08	<0.026
24-5	23-29	0.076572	<0.006	0.162716	0.089015	<0.08	<0.026
26-1	0-4	0.05048	<0.006	0.232207	0.026249	<0.08	<0.026
26-2	10-14	<0.003	<0.006	0.220738	0.03679	<0.08	<0.026
26-4	20-24	0.336674	<0.006	0.060429	<0.0017	<0.08	<0.026
26-5	24-25	<0.003	<0.006	1.544038	0.085675	<0.08	<0.026
28-1	0-6	<0.003	<0.006	0.238124	0.09472	0.513644	<0.026
28-2	6-15	<0.003	<0.006	0.211583	0.217629	<0.08	<0.026
28-3	15-19.5	0.059943	<0.006	<0.007	0.011132	<0.08	<0.026
30-1	0-3	0.037753	<0.006	0.122698	0.069843	<0.08	<0.026
30-3	15.5-18	0.278083	<0.006	<0.007	0.07322	0.126513	<0.026
30-4	18-26.5	<0.003	0.136114	<0.007	<0.0017	<0.08	<0.026
30-5	30-31.5	0.392968	<0.006	<0.007	0.021832	<0.08	<0.026
31-2	3-10	<0.003	<0.006	<0.007	<0.0017	<0.08	<0.026
31-3	10-20	0.096863	<0.006	0.242158	<0.0017	1.017065	<0.026
31-4	25-30.5	0.124503	<0.006	<0.007	<0.0017	<0.08	<0.026
32-1	0-7	<0.003	<0.006	<0.007	<0.0017	<0.08	<0.026
32-3	15-21	0.366839	<0.006	<0.007	<0.0017	0.383901	<0.026
32-4	21-26.5	0.111849	<0.006	<0.007	<0.0017	2.635549	<0.026
33b-1	0-5	0.213956	<0.006	<0.007	<0.0017	<0.08	<0.026
33b-3	13.5-19	0.089967	<0.006	<0.007	0.007636	<0.08	<0.026
34a3	17-22	<0.003	<0.006	<0.007	<0.0017	<0.08	<0.026
34a4	27-31.5	<0.003	<0.006	<0.007	<0.0017	<0.08	<0.026
38-2	8.5-11	0.01728	<0.006	<0.007	<0.0017	<0.08	<0.026
38-3	11-17	0.250209	<0.006	<0.007	<0.0017	<0.08	<0.026
37-3	10.5-19	0.175002	<0.006	<0.007	<0.0017	<0.08	<0.026
%ERROR		12.89	N.A.	8.15	14.61	21.23	29.15

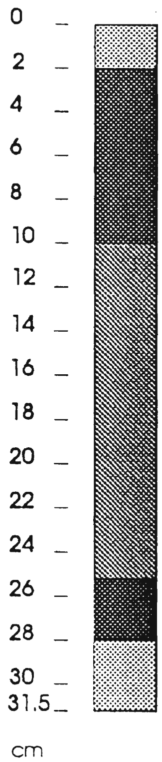
TPH (Total Petroleum Hydrocarbons)
O & G (Oil and Grease) Provincial Sediment Guilines Max 1500m g/kg.

Core	Depth Cm	TPH(mg/kg)	Core	Depth Cm	TPH(mg/kg)
Opt1-2	4-2	*2680	Wrk2-1	0-5	373
Opt1-4	17.5-19	*1942	Wrk2-3	5-14	661
Opt1-7	33-34	1013	Wrk2-4	27.5-30	296
7-3	13-15	*2800	Wrk3-1	0-4.5	*4270
7-4	22-25	*1646	Wrk3-2	4.5-9.5	*1860
7-7	41-42.5	861	1cr	4.8-9.1	30
2-1	0-2	793	1cr	14.9-19.5	22
2-5	39-40	*4491	1cr	24.5-29.5	< 14
2-7	64-66.5	*2758	2cr	3.2-5.3	< 14
4-3	17-18	1421	2cr	5.3-8.3	228
4-5	31-32	*1883	2cr	8.3-11.7	< 14
4-10	83-85	1421	23-5	24.5-30	938
6-2	9-11	*5971	24-3	10-15	117
6-6	63-65	827	25-2	6.5-10.5	*2675
6-10	87-89	*4478	26-3	17-20	626
1day-2	8.5-10	1010	26-5	24-25	*3008
1day-7	57-58	*1985	27-1	0-3	*4398
1day-8	61-62	672	27-3	5.5-14	*4316
5-2	4-5	252	27-4	14-17	*4438
5-6	26-28	*1737	28-2	6-15	53
5-7	46-47	1463	29-1	0-5.5	372
5-10	79-81	496	31-2	3-10	< 14
a2	2-8	*1560	31-3	10-20	< 14
a5	25.5-28	558	30-3	15.5-18	173
22-2	6.5-9	*3708	30-5	30-31.5	< 14
22-3	15-20	*2763	32-3	15-21	< 14
21-2	5-12	387	32-4	21-26.5	< 14
b4	13.5-19.5	1180	34c-2	3-11.5	< 14
b6	24.5-30.5	567	34b-2	8-16	< 14
c3	6.5-11.5	1461	37-1	0-3.5	236
c7	24-31.5	14	38-2	8.5-11	252
20-1	0-4	556	39-1	0-6	*20646
19-3	7-10.5	*5542	39-3	15-20.5	*24834
IC1-1	0-1	1122	39-5	29-31.5	*11256

%Recovery	95
%Error	14.55

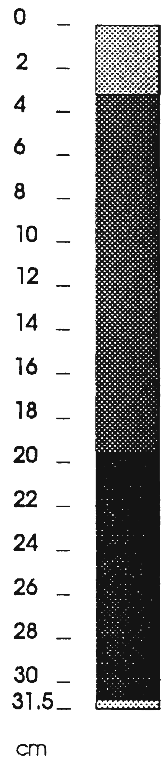
* TPH > Oil & Grease MOEE guidelines.

Core A



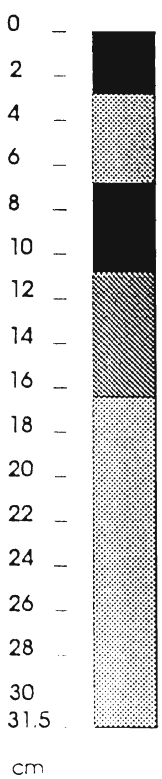
Description	Sample	Sample Interval
Sandy brown clay	A1	0-2
Dark grey clay High peat content	A2	2-8
Light grey clay Very high in peat	A3	8-16
	A4	16-25.5
Dark brown clay High peat content	A5	25.5-28
Light grey clay	A6	28-31.5

Core B



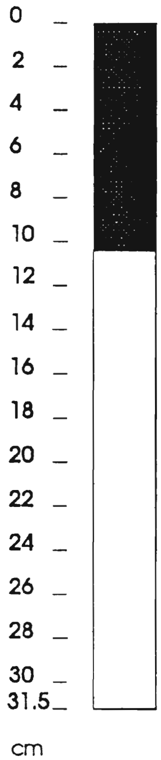
Description	Sample	Sample Interval
Light brown clay	B1	0-3
Dark brown clay	B2	3-8
	B3	8-13.5
	B4	15-19.5
Dark grey/black clay thin light grey lens	B5	19.5-24.5
	B6	24-30.5
Light grey clay	B7	30.5-31.5

Core C



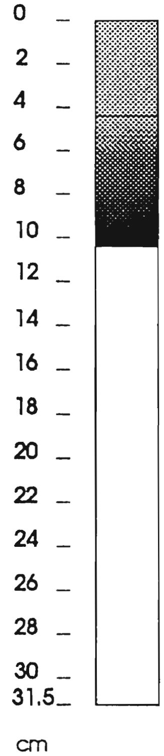
Description	Sample	Sample Interval
Dark black silty clay very high in peat	C1	0-2
Light brown clay minor peat content	C2	2-6
Dark black clay	C3	6.5-11.5
Light brown sandy clay with minor peat content	C4	11.5-14
	C5	14-16
Light brown/grey clay	C6	16-24
	C7	24-31.5

Core 18



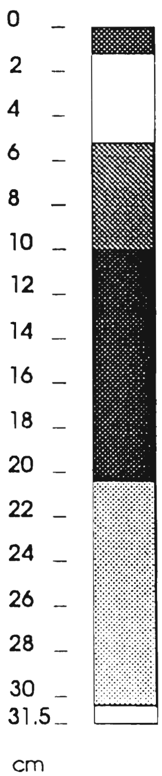
Description	Sample	Sample Interval
	18-1	0-3
Homogenius black clay with some pulp like material	18-2	3-6
	18-3	7-10.5

Core 19



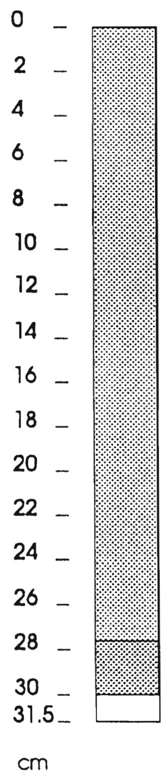
Description	Sample	Sample Interval
Light brown sandy clay high in pulp like material	19-1	0-3
Light grey clay grading into black clay downwards with less pulp like material	19-2	3-7
	19-3	7-10.5

Core IC1



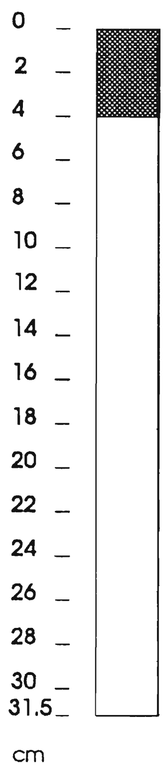
Description	Sample	Sample Interval
Dark grey sandy clay high in peat	IC-1	0-1
Gas Pocket		
Medium brown sandy clay		
Dark grey clay high in peat and pulp like material		
Light grey clay high in peat and pulp like material		

Core WRK2



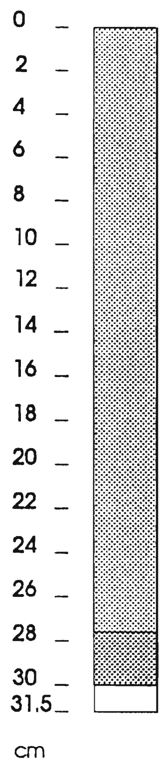
Description	Sample	Sample Interval
Light brown clay with no visible peat	WRK2-1	0-5
	WRK2-2	5-14
Light brown sandy clay	WRK2-3	27.5-30

Core 20



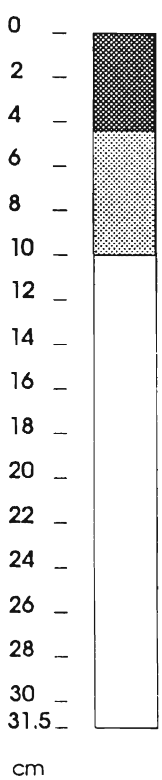
Description	Sample	Sample Interval
Dark grey sandy clay	20-1	0-4

Core WRK2



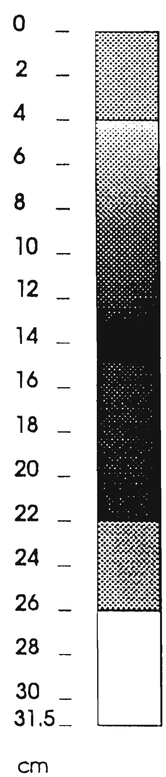
Description	Sample	Sample Interval
Light brown clay with no visible peat	WRK2-1	0-5
	WRK2-2	5-14
Light brown sandy clay	WRK2-3	27.5-30

Core WRK3



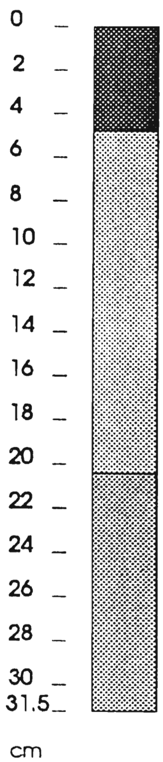
Description	Sample	Sample Interval
Dark grey silty sand, very high in peat and pulp like material	WRK3-1	0-4.5
Light brown sandy clay high in pulp	WRK3-2	4.5-9.5

Lake St. Clair



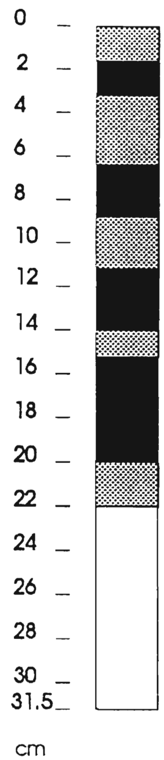
Description	Sample	Sample Interval
Light brown sandy clay with zebra mussel shells	St.Cl 1	0-4
Light brown sandy clay grading downwards into darker less sandy clay with diminishing zebra mussel shells	St. Cl 2	4-8
Dark black clay high in peat with no zebra mussel shells	St. Cl 3	8-16
Light brown sandy clay with no peat	St. Cl 4	16-22

Core 21



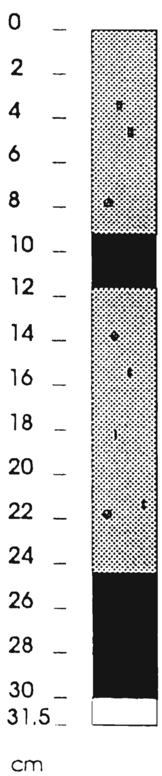
Description	Sample	Sample Interval
Dark brown/black clay very high in peat	21-1	0-5
Light brown clay moderately high in peat	21-2	5-12
	21-3	12-20.5
Light brown/grey clay	21-4	20.5-26
	21-5	26-30.5

Core 22



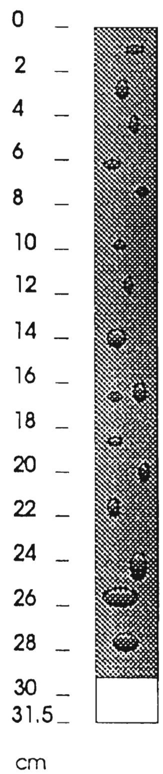
Description	Sample	Sample Interval
Light brown and black banded sandy clay as shown	22-1	0-1.5
	22-2	6.5-9
	22-3	15-20
	22-4	20-22

Core 23



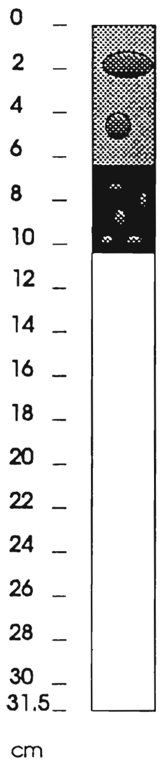
Description	Sample	Sample Interval
Light brown sandy clay high in peat content with some pebbles <1.5mm	23-1	0-9
Black clay high in organics	23-2	9-11.5
Light brown sandy clay with some minor pebbles <1mm	23-3	12-17
	23-4	17-24.5
Dark black sandy clay	23-5	24.5-30

Core 24



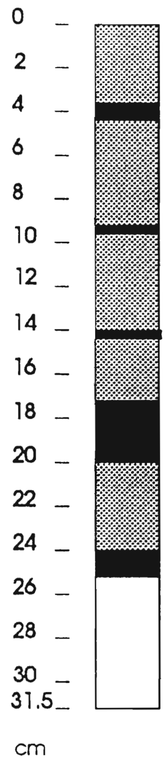
Description	Sample	Sample Interval
Medium light brown sandy clay with pebbles coarsening downwards >2mm <8mm	24-1	0-4
	24-2	4-10
	24-3	10-15
	24-4	15-23
	24-5	23-29

Core 25



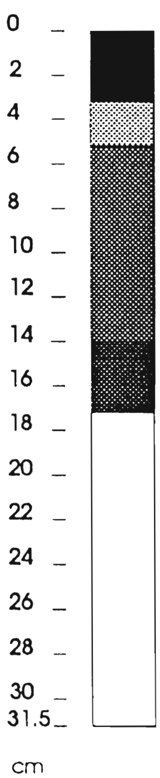
Description	Sample	Sample Interval
Light brown sandy clay with some peat and slag like particles >1.5 cm	25-1	0-6.5
Dark black sandy clay high in slag like particle (>5mm) content	25-2	6.5-10.5

Core 26



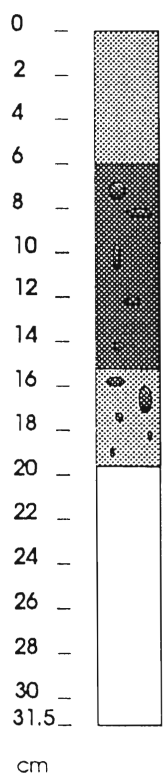
Description	Sample	Sample Interval
Light brown silty clay intermixed with dark organic rich lenses as shown	26-1	0-4
	26-2	10-14
	26-3	17-20
	26-4	20-24
	26-5	24-25

Core 27



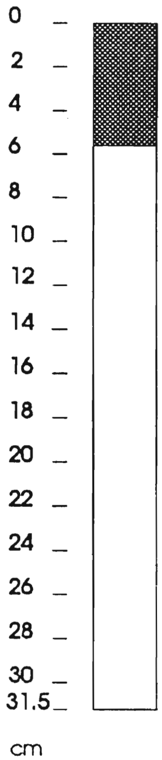
Description	Sample	Sample Interval
Dark black sandy clay	27-1	0-3
Light brown sandy clay	27-2	3-5.5
Medium brown sandy clay high in peat content	27-3	5.5-14
Dark brown sandy clay very high in peat	27-4	14-17

Core 28



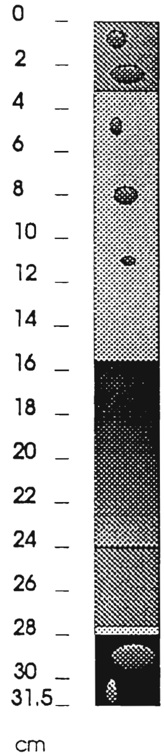
Description	Sample	Sample Interval
Light brown sandy clay	28-1	0-6
Dark brown sandy clay high in peat content and some pebbles >3mm	28-2	6-15
Light brown sandy clay low in peat and pebbles >3mm finning downwards	28-3	15-19.5

Core 29



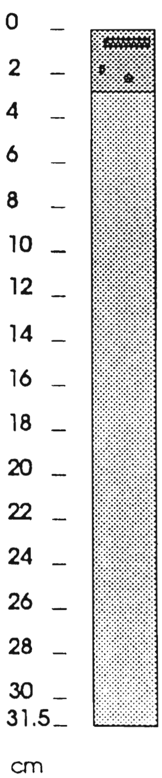
Description	Sample	Sample Interval
Homogenius medium brown clay	29-1	0-5.5

Core 30



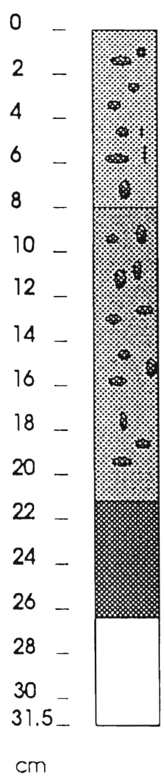
Description	Sample	Sample Interval
Medium brown clay with some minor sand and pebbles >3mm <5mm	30-1	0-3
Light brown sandy clay with some minor pebbles >2mm	30-2	3-10
Black sandy clay high in peat content lightening dowards	30-3	15.5-18
Light brown sandy clay	30-4	18-26.5
Very light brown clay lens		
Black sandy clay with pebbles >3cm <5cm	30-5	30-31.5

Core 31



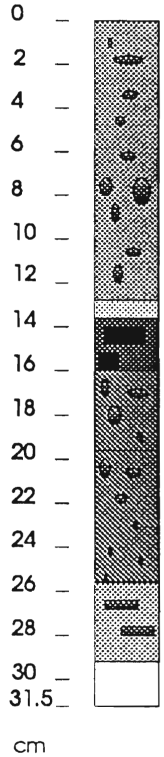
Description	Sample	Sample Interval
Light brown clay with slag like fragments >3cm and pebbles <5mm	31-1	0-3
	31-2	3-10
Light grey sandy clay coarsening downwards		
	31-3	10-20
	31-4	25-30.5

Core 32



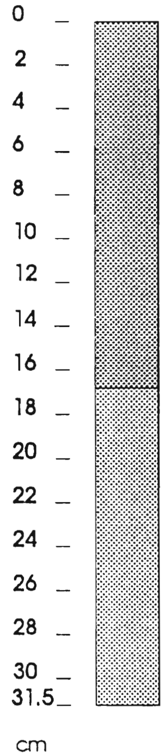
Description	Sample	Sample Interval
Light brown homogenius silty clay high in pebble content >2mm	32-1	0-7
	32-2	10-15
Medium brown/grey clay very high in pebble content >2mm with some sand sized particles <1mm		
	32-3	15-21
Medium brown clay intermixed with dark black clasts of sandy clay	32-4	21-26.5

Core 33



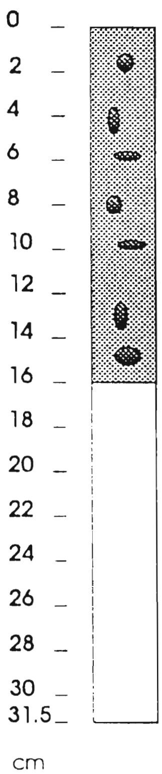
Description	Sample	Sample Interval
Light brown sandy clay with pebbles >1mm and <3mm fining downwards	33-1	0-5
	33-2	5-13.5
Light grey clay lens		
Black clay with large wood inclusions	33-3	13.5-19
Medium black clay with pebbles >2mm <5mm		
Medium black clay with pebbles <3mm fining downwards into a sandy black clay		
Light brown sandy clay with wood chips 80%	33-4	26-29

Core 34A



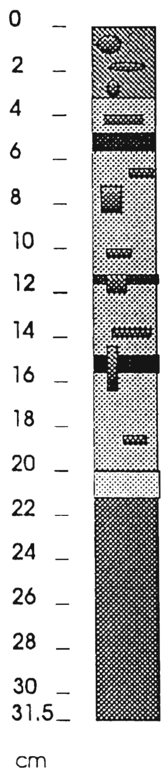
Description	Sample	Sample Interval
Light brown sand fining downwards	34A-1	0-5
	34A-2	12-17
Very sharp contact as shown.	34A-3	17-22
Light grey clay		
	34A-4	27-31.5

Core 34B



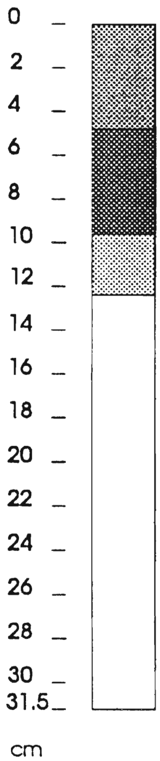
Description	Sample	Sample Interval
Light brown very sandy clay with pebbles >1mm <2.5mm	34B-1	0-8
	34B-2	8-16

Core 34C



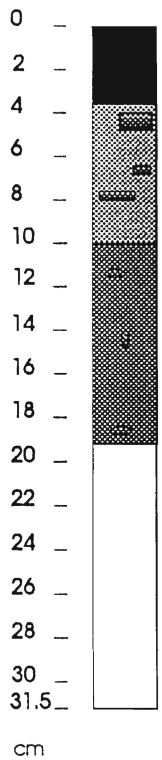
Description	Sample	Sample Interval
Medium brown clay with large pebbles >3mm fining downwards	34C-1	0-3
Light brown clay intermixed with large wood fragments and high in peat content. Dark black clay lens occurred as shown	34C-2	3-11.5
	34C-3	11.5-20
Light grey clay lens		
Medium to dark brown sandy clay	34C-4	20-31

Core 35



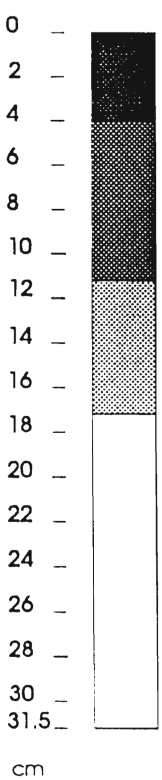
Description	Sample	Sample Interval
Light brown sand	35-1	0-5
Medium brown sandy silt intermixed with twigs	35-2	5-9.5
Light brown sand	35-3	9.5-12.5

Core 37



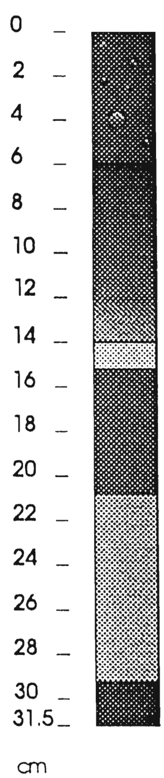
Description	Sample	Sample Interval
Dark black sandy clay	37-1	0-3.5
Light brown clay interlaced with thin lens of dark black sandy clay high in peat and brick fragments	37-2	8-10.5
Medium brown sandy clay with minor pebble content >2mm	37-3	10.5-19

Core 38

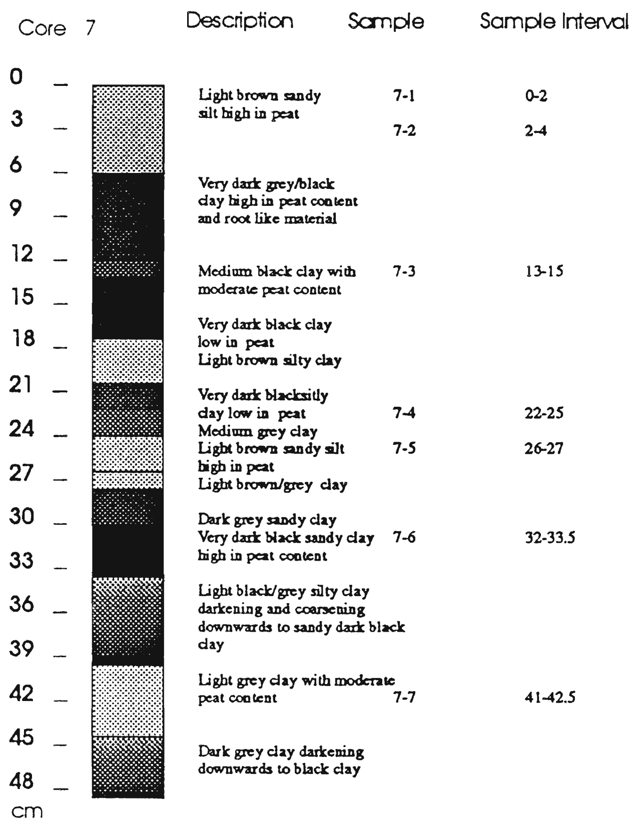


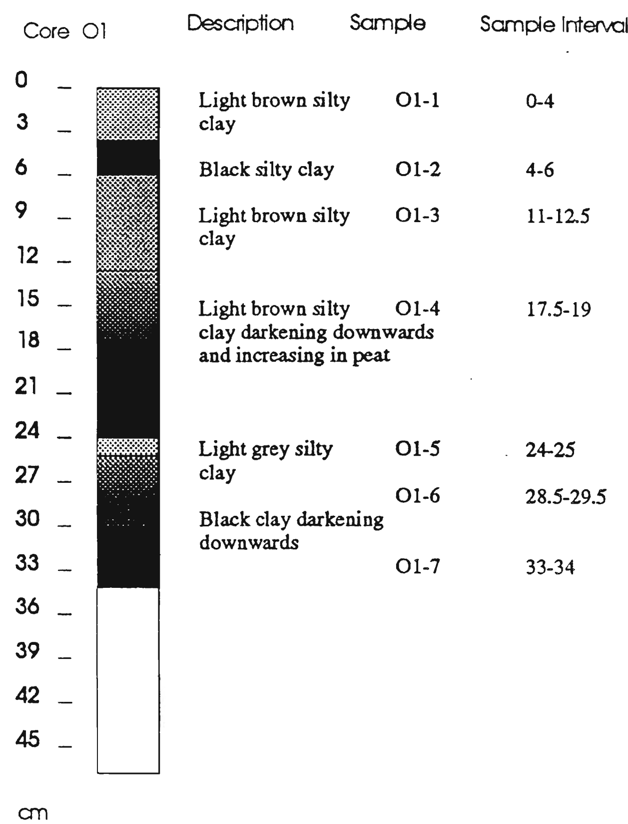
Description	Sample	Sample Interval
Black sandy clay with high peat content and zebra mussel shell content	38-1	0-4
Medium black clay high in peat with no zebra mussel shells	38-2	8.5-11
Light brown sandy clay with no visible organic matter or zebra mussel shells	38-3	11-17

Core 39

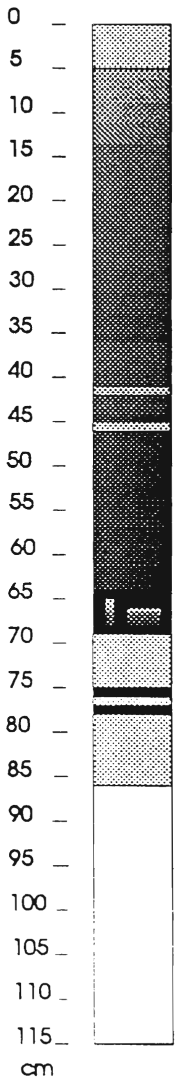


Description	Sample	Sample Interval
Dark brown/black clay high in peat with some pebbles >0.5mm coarsing downwards	39-1	0-6
Dark brown/black clay high in peat with intermixed sand sized particles <0.5mm	39-2	6-14
Light grey clay	39-3	15-20.5
Dark brown clay high in peat content with silt coarsing downwards into sand	39-4	20.5-29
Light brown clay low in peat		
Dark brown clay very high in peat	39-5	29-31.5


Core 7
Description
Sample
Sample Interval
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
cm
Light brown sandy silt high in peat
7-1
0-2
7-2
2-4
Very dark grey/black clay high in peat content and root like material
Medium black clay with moderate peat content
7-3
13-15
Very dark black clay low in peat
Light brown silty clay
Very dark blacksitly clay low in peat
7-4
22-25
Medium grey clay
Light brown sandy silt high in peat
7-5
26-27
Light brown/grey clay
Dark grey sandy clay
Very dark black sandy clay high in peat content
7-6
32-33.5
Light black/grey silty clay darkening and coarsening downwards to sandy dark black clay
Light grey clay with moderate peat content
7-7
41-42.5
Dark grey clay darkening downwards to black clay

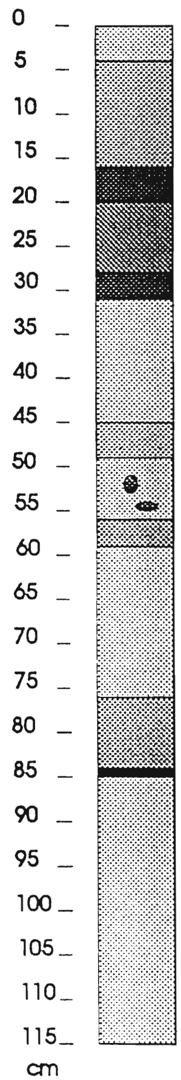

Core O1
Description
Sample
Sample Interval
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
cm
Light brown silty clay
O1-1
0-4
Black silty clay
O1-2
4-6
Light brown silty clay
O1-3
11-12.5
Light brown silty clay darkening downwards and increasing in peat
O1-4
17.5-19
Light grey silty clay
O1-5
24-25
O1-6
28.5-29.5
Black clay darkening downwards
O1-7
33-34

Core 2

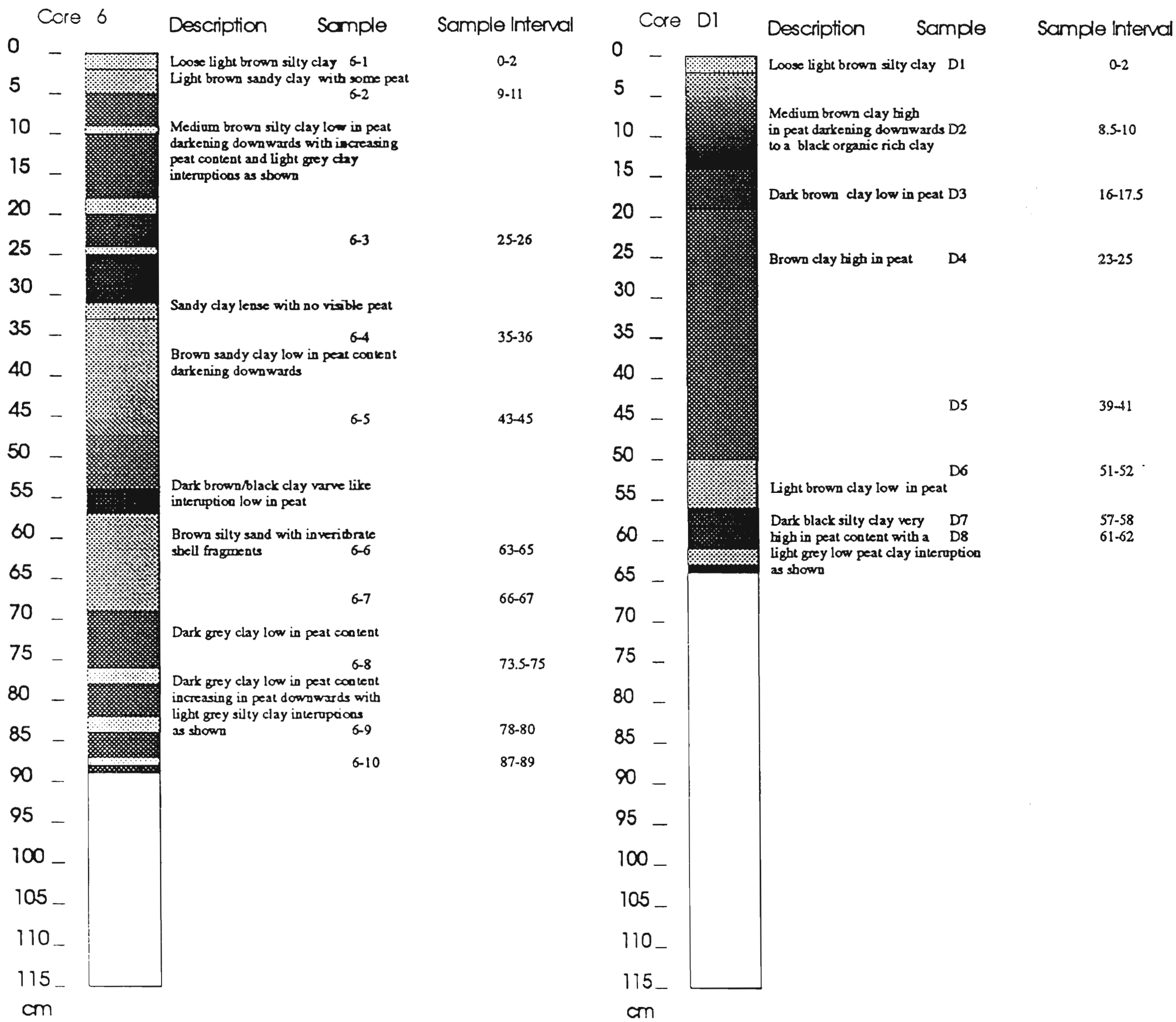


Description	Sample	Sample Interval
Light brown silty clay	2-1	0-2
Light brown silty clay darkening downwards with no visible peat	2-2	2-4
	2-3	24-26
	2-4	33-34
Dark grey organic rich clay with light grey clay interuptions as shown and darkening downwards	2-5	39-40
	2-6	54.5-56
Very dark organic rich clay with coal inclusions and high in peat content	2-7	64-66.5
Light grey clay with dark peat lenses as shown	2-8	72-73
	2-9	80-82

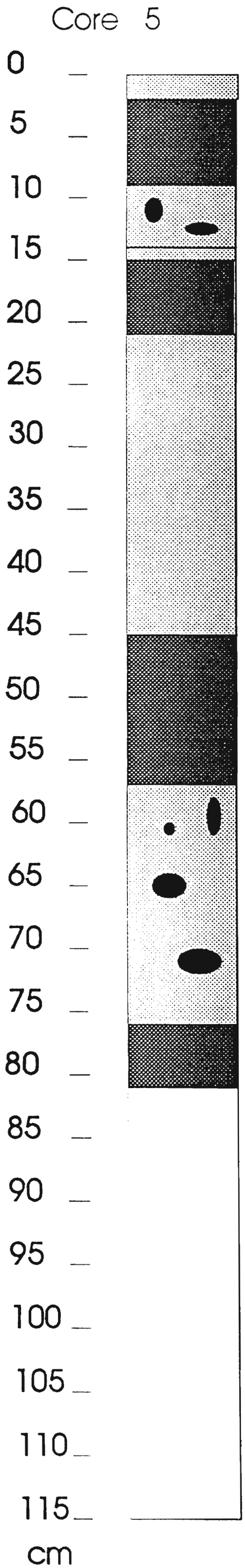
Core 4



Description	Sample	Sample Interval
Light brown loose silty clay	4-1	0-3
	4-2	3-5
Light to medium brown clay		
Dark brown/black silty clay	4-3	17-18
Medium brown sandy clay	4-4	23-24
Dark brown/black silty clay	4-5	31-32
Light grey sandy clay		
Medium brown silty sand	4-6	46.5-48
Light grey sandy clay with sandy clasts		
Medium brown silty sand		
Light grey sandy clay	4-7	61-63
	4-8	72-73
Medium brown silty sand	4-9	78-79
	4-10	83-85
Dark peat lens		
Light grey sandy clay		
	4-11	98-100
	4-12	108-110



Core 6
Description
Sample
Sample Interval
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
cm
Loose light brown silty clay 6-1 0-2
Light brown sandy clay with some peat
6-2 9-11
Medium brown silty clay low in peat darkening downwards with increasing peat content and light grey clay interuptions as shown
6-3 25-26
Sandy clay lense with no visible peat
6-4 35-36
Brown sandy clay low in peat content darkening downwards
6-5 43-45
Dark brown/black clay varve like interuption low in peat
Brown silty sand with inveritbrate shell fragments 6-6 63-65
6-7 66-67
Dark grey clay low in peat content
6-8 73.5-75
Dark grey clay low in peat content increasing in peat downwards with light grey silty clay interupotions as shown 6-9 78-80
6-10 87-89
Core D1
Description
Sample
Sample Interval
Loose light brown silty clay D1 0-2
Medium brown clay high in peat darkening downwards D2 8.5-10
to a black organic rich clay
Dark brown clay low in peat D3 16-17.5
Brown clay high in peat D4 23-25
D5 39-41
D6 51-52
Light brown clay low in peat
Dark black silty clay very D7 57-58
high in peat content with a D8 61-62
light grey low peat clay interuption as shown



Description	Sample	Sample Interval
Loose light brown clay high in peat	5-1	0-2
Very dark brown silty clay high in peat	5-2	4-5
	5-3	7-8
Light brown silty clay low in peat with black organic rich clasts	5-4	9-10
	5-5	10.5-11.5
Light brown silty clay low in peat		
Very black silty clay high in peat		
Light brown silty clay low in peat	5-6	26-28
Dark brown silty clay low in peat	5-7	46-47
Light brown silty clay low in peat with black organic rich clasts		
	5-8	70-71
	5-9	75-76
Dark brown silty clay high in peat content	5-10	79-81

APPENDIX 2

EXPERIMENTAL DATA AND PASSIVE BIOMONITORING

Acid/Time Oven/Shaker Experiment.
Using Mytilus Edulis Oven Dried Tissue

Acid Strength % V/V	Time	Oven pb(ppb)	Shaker pb(ppb)	Oven zn(ppm)	Shaker zn(ppm)	Oven cd(ppm)	Shaker cd(ppm)
10	72hr	62.22	79.52	1.91	1.60	0.0517	0.0760
5	72hr	80.60	71.25	1.71	1.49	0.0617	0.0433
2.5	72hr	50.01	40.86	1.46	1.43	0.0243	0.0257
1.3	72hr	26.90	25.62	1.55	1.32	0.0293	0.0283
0.5	72hr	32.64	53.55	1.86	1.51	0.0330	0.0283
0.25	72hr	59.91	38.74	1.50	1.29	0.0263	0.0237
10	24hr	21.17	39.61	1.33	1.30	0.0257	0.0250
5	24hr	27.96	26.66	1.31	1.09	0.0280	0.0237
10	4hr	19.99	13.31	0.99	0.59	0.0177	0.0093
5	4hr	57.22	17.85	1.40	0.50	0.0253	0.0083

Histochemical location of 30 Zebra Mussels 2.7-3.2cm size class
(All values in ppm) Site 10 (Martindale Pond/30 day lab mussels)

	res	mus/kid	foot+bys	gut/kid	gills
Cu	7.169	3.855	0	9.017	9.218
Ni	9.129	11.108	24.738	9.58	22.758
Pb	1.156	0.964	8.851	0.905	0
Cd	0.72	0.89	1.48	2.39	1.15
Zn	76.35	368.6	118.28	67.73	97.87

Note: res = residual (mantle, gonads and digestive gland)
mus/kid = muscle with some kidney
foot+bys = foot and byssus
gut/kid = gut with some kidney

Passive Zebra Mussel (Zm) and Quagga Mussel(Qm) Comparison Data — All values ppm unless otherwise stated.

Qm comparison

sample Date			Length	Sample Size	Cu	Ni	Zn	Cd	Al	Cr	As(ppb)	Pb(ppb)	Se(ppb)	Co(ppb)	Be(PPB)
Oct/94	Pt Col.Hbr	Q.m	2-2.5	30	13.45899	5.781723	134.1231	0.827502	50.46775	0.97787	1775.213	2144.178	1545.248	1.746196	
Nov/94	site 10 Q	Q.m	2.5-3	14	8.702864	2.636629	116.3122	1.037025	95.15738	1.502534	2153.971	1586.132	1010.775		
Dec/94	site16 Qm	Q.m.	1.5-2	24	15.51253	3.679888	86.42869	0.443204	233.0884	1.990688	6483.104	4635.78	1815.88		
Dec/94	site16 Qm	Q.m.	2-2.5	27	11.51349	3.167727	69.45986	0.378927	199.5965	1.489694	6299.951	2980.258	1852.05		
Dec/94	site16 Qm	Q.m.	2.5-3	10	10.48023	4.172398	48.18114	0.323945	165.5755	3.553672	2010.863	3416.245	1173.552		
Nov/94	gibs Qm 1.	Q.m.	1.5-2	20	20.28974	3.718834	91.61688	1.051844	84.10107	4.057382	3477.56	2857.606	4651.175		
Nov/94	gibs Qm 2	Q.m.	2-2.5	15	19.00834	5.412861	100.2503	0.810113	115.6136	3.78197	3132.746	2298.46	4299.881		
Nov/94	gibs Qm 2.	Q.m.	2.5-3	14	18.86274	6.436246	110.3909	1.085176	243.3189	3.67481	2804.264	3458.326	3315.666		
	%ERROR				4.147095	4.583877	7.036289	8.927743	10.45498	11.39039	21.12605	20.25413	18.79697		

Zm comparision

sample Date			Length	Sample Size	Cu	Ni	Zn	Cd	Al	Cr	As(ppb)	Pb(ppb)	Se(ppb)	Co(ppb)	Be(PPB)
Oct/94	Pt Col.Hbr	Z.m	2.5-3	14	14.47551	27.15134	122.3945	1.480189	52.24173	1.491409	3739.709	1362.748	2371.143	354.3754	78.80278
Nov/94	site 10 Z	Z.m	2.5-3	30	8.055039	5.686507	95.74751	0.573919	34.99196	1.13501	1336.521	482.3212	2096.32	173.6856	
Dec/94	site 10 Z	Z.m	3-3.25	30	14.06863	12.48554	140.6423	14.0399	19.96776	1.200721	2021.38	22475.78	2112.941		1118.998
Dec/94	site16 Zm	Z.m	1.5-2	28	14.08514	4.057548	62.04758	0.097081	151.5538	3.820244	2847.622	3485.175	2417.997		
Dec/94	site16 Zm	Z.m	2-2.5	27	11.91582	4.827352	66.85606	0.207982	116.5166	2.966547	3895.751	2773.828	2765.253		
Dec/94	site16 Zm	Z.m	2.5-3	30	12.53417	6.288929	70.38472	0.374682	127.3755	2.36229	3043.803	3919.044	3172.463		
Dec/94	site16 Zm	Z.m	3-3.5	12	11.8041	5.818896	71.25698	0.414621	97.4933	2.311361	3048.409	3343.177	854.3063		
Nov/94	gibs Zm 1.	Z.m.	1.5-2	30	21.47813	5.529606	95.86148	0.794791	93.05747	3.164093	1391.973	2366.65	4701.758		
Nov/94	gibs Zm 2-	Z.m.	2-2.5	23	18.65517	7.788809	108.2919	0.913775	98.28667	4.106287	2198.436	2673.862	5859.616		
Nov/94	gibs Zm 2.	Z.m.	2.5-3	26	19.97441	9.563937	109.48	1.041004	117.8276	4.846566	3782.911	2328.438	5130.127		
Nov/94	gibs Zm 3-	Z.m.	3-3.5	17	19.32863	13.25414	109.8401	1.025007	155.4728	5.846488	5192.907	2725.989	5250.467		
ZM	%ERROR				3.249291	4.552416	2.859425	11.55056	13.2738	8.397349	23.47222	19.86356	24.55417		

Lake St. Clair (Jeanette's Creek Chattam Ontario)
Passive Zebra Mussel Biomonitoring Sampled Oct 15/94

Length	Sample Size	Cu	Ni	Zn	Cd	Al	Cr	As	Pb	Se	Co	Be(ppb)	Mo
>3.5	28	10.5232	5.696641	76.63399	0.301499	89.20332	1.904338	2.398729	15.78644	2.441707	0.673577	15.45731	2.062706
3-3.5	30	9.381093	7.495944	84.85218	0.829568	104.2589	1.910467	2.588928	18.48292	1.78322	0.498155	5.066458	1.396271
2.5-3	30	9.119545	6.363976	86.34551	0.493674	161.1606	2.485889	2.808166	11.8143	2.162483	0.603392	5.209535	0.752033
2-2.5	30	8.638091	5.651801	79.48842	0.445729	107.9178	1.555706	1.430217	14.28022	2.351254	0.640061	7.442022	0.89733
%Error		8.31	7.66	5.69	16.64	19.86	22.47	44.35	28.48	14.42	20.04	25.28	26.22

Big Reference Clams Sampled from Johnston Harbour Tobermory Ontario Sept 94
Ana = Anadonta sp.
Ell = Elliptio sp.

( )= quantity	Cu	Ni	Zn	Cd	Al	Cr	Mo(ppb)	Be(ppb)	As(ppb)	Co(ppb)	Se(ppb)	Pb(ppb)	Length cm	Breadth cm
Ana 132cm (1)														
Kidney	7.96	12.79	227.00	72.11	<MDL	<MDL	1763	<MDL	19441	22122	15290	25325	136.00	54.60
Gill with ovary	6.35	18.46	265.87	1.01	1.25	<MDL	2155	<MDL	3497	2151	1013	8246	136.00	54.60
Muscl	1.52	2.00	96.33	1.45	<MDL	<MDL	<MDL	<MDL	2881	<MDL	6232	5058	136.00	54.60
Gut	6.70	2.26	108.49	5.71	19.80	1.19	270	<MDL	8158	1103	8676	7164	136.00	54.60
Heart & Rectum	<MDL	1.33	87.71	<MDL	<MDL	<MDL	<MDL	<MDL	7010	<MDL	9436	47727	136.00	54.60
Foot with ovary	4.30	4.77	118.90	0.84	<MDL	<MDL	4077	<MDL	1441	<MDL	5916	9593	136.00	54.60
Mantle	4.87	<MDL	141.45	9.11	26.22	4.37	<MDL	<MDL	5293	<MDL	5568	6819	136.00	54.60
Ana 117.5-120 (2)														
Kid with man/Gill	18.66	<MDL	552.16	41.62	78.07	<MDL	1535	<MDL	1084	<MDL	9038	16686	120.00	46.00
Gill with ovary	9.43	4.42	342.82	<MDL	40.40	<MDL	14254	151	1347	<MDL	635	7180	120.00	46.00
Muscl	0.90	<MDL	104.54	3.90	72.09	<MDL	<MDL	<MDL	2814	<MDL	7801	4008	120.00	46.00
Gut	6.69	0.11	126.47	4.76	25.16	0.57	145583	<MDL	4695	563	5391	1983	120.00	46.00
Heart & Rectum	1.63	<MDL	65.70	0.81	<MDL	<MDL	295914	<MDL	4860	<MDL	2063	26818	120.00	46.00
Foot	5.30	2.04	129.81	3.75	8.66	2.23	12463	53	4268	<MDL	4755	3588	120.00	46.00
Ana 102.5-111.5 (3)														
Kid with gill/man	12.82	1.71	311.01	70.62	11.32	6.83	3940	602	22277	10139	12977	15461	109.40	43.60
Gill	20.68	9.51	598.31	6.09	15.12	4.36	4732	262	7308	2212	2187	27586	109.40	43.60
Muscl	1.02	<MDL	72.69	0.89	15.04	<MDL	3358	<MDL	7046	1127	4874	6549	109.40	43.60
Gut	7.98	1.48	104.99	3.34	16.02	<MDL	690	<MDL	6125	332	7939	2910	109.40	43.60
Heart & Rectum	<MDL	<MDL	153.44	6.87	<MDL	0.26	<MDL	<MDL	25082	<MDL	3048	16121	109.40	43.60
Foot	6.74	<MDL	112.14	0.98	3.77	<MDL	<MDL	<MDL	5706	<MDL	8059	3187	109.40	43.60
Mantle	9.73	1.18	180.95	8.03	21.88	<MDL	269	<MDL	7060	865	13178	3419	109.40	43.60
Ana 100 cm (1)														
Kidney	19.61	5.88	355.95	118.26	9.81	0.25	6271	<MDL	8874	3898	3849	1246	100.00	41.00
Gill	48.01	9.06	506.70	26.79	16.90	7.51	4492	338	2025	1437	2360	13955	100.00	41.00
Muscl	1.24	<MDL	61.82	1.91	8.13	<MDL	1911	<MDL	5781	198	2070	3413	100.00	41.00
Gut	13.31	2.34	144.23	11.82	4.57	1.56	460	260	3505	158	2341	6541	100.00	41.00
Heart & Rectum	<MDL	<MDL	122.88	20.01	<MDL	14.43	4681	<MDL	63160	4561	15173	77132	100.00	41.00
Foot	8.69	<MDL	120.95	4.45	<MDL	<MDL	200	<MDL	2440	<MDL	3079	2090	100.00	41.00
Mantle	11.13	0.75	170.15	18.82	<MDL	2.89	3519	<MDL	5256	300	3442	2329	100.00	41.00
Ell 92-105 (2)														
Kid with man/gill	7.66	6.98	367.27	131.05	49.55	<MDL	10711	<MDL	33537	68496	29415	23397	96.50	41.00
Gill with ovary	18.68	11.16	491.45	2.50	33.90	<MDL	3943	1021	5461	1820	3859	1635	96.50	41.00
Muscl	1.92	0.11	149.44	2.09	6.52	0.34	4057	<MDL	6844	<MDL	665	651	96.50	41.00
Gut	5.60	6.98	476.33	2.78	6.39	5.23	3052	317	5740	1519	1503	9700	96.50	41.00
Heart & Rectum	7.01	3.21	611.69	3.15	<MDL	6.42	540	31	5415	<MDL	<MDL	13963	96.50	41.00
Foot	2.02	<MDL	110.93	1.99	<MDL	<MDL	380	<MDL	3411	329	2144	1652	96.50	41.00
Mantle	4.30	7.76	673.36	2.70	4.62	5.53	1268	151	591	984	3267	28309	96.50	41.00

% Errors Values

	Cu	Ni	Cd	Al	Cr	Zn	As(PPB)	Pb(PPB)	Mo(PPB)	Be(PPB)	Co(PPB)	Se(PPB)
muscl avg %error	15.30	N.A.	18.33	16.43	N.A.	5.96	45.91	47.19	81.94	N.A.	29.71	26.78
mant avg %error	2.47	24.81	0.38	24.20	8.82	17.01	8.74	7.19	5.33	9.49	33.02	27.88
Kidney avg %error	16.59	49.82	1.12	48.69	10.04	3.25	26.20	33.10	19.81	N.A.	27.09	19.12
Gut avg %error	6.29	39.52	2.35	31.08	23.24	2.98	17.35	33.12	19.16	12.69	30.86	27.62
Gill avg %error	19.36	7.61	2.54	9.01	9.46	2.65	18.52	24.11	15.70	25.72	58.17	25.30
Foot avg %error	12.48	N.A.	26.56	N.A.	N.A.	4.73	33.36	17.74	88.29	N.A.	N.A.	28.90
Element %Error	12.08	30.44	8.54	25.88	12.89	6.10	25.02	27.07	38.37	15.96	35.77	26.26

APPENDIX 3

ACTIVE BIOMONITORING

Active Biomonitors   All values are ppm unless otherwise stated.

After 69 days

Zm

		Cu	Ni	Cd	Al	Cr	Zn	Pb(ppb)	As(ppb)	Se(ppb)
Decew		12.09	28.53	1.90	1041.01	1.58	102.89	4178	731	2521
Glendale		11.34	34.54	1.47	926.75	2.69	99.90	4438	163	866
N.C.		10.72	29.06	1.50	458.61	1.36	98.66	4059	<MDL	840
Site 10		10.59	16.71	1.13	726.21	7.09	81.05	3895	<MDL	1315
Site 16		9.92	34.94	1.05	475.95	4.89	98.09	4735	1629	1096
Lake Gibson		22.17	21.98	1.43	349.17	3.29	111.15	2816	1435	238
Capri		14.06	32.27	1.66	727.93	2.12	171.91	13286	<MDL	823
	%ERROR	7.50	9.28	3.06	11.16	31.44	3.98	26	44	36

After 69 days

Qm

		Cu	Ni	Cd	Al	Cr	Zn	Pb(ppb)	As(ppb)	Se(ppb)
Decew		9.86	9.55	1.37	862.79	1.18	62.57	3665	2365	2880
Glendale		9.66	8.40	1.22	1140.51	1.47	68.32	4026	739	1060
N.C.		9.88	9.87	0.81	872.24	0.68	60.18	4584	1337	2167
Site 10		9.43	14.85	1.00	638.29	29.24	74.05	2789	1114	<MDL
Site 16		8.91	8.72	0.70	1152.86	1.88	55.44	5479	1823	<MDL
Lake Gibson		11.06	6.75	1.08	704.29	6.74	86.67	4546	1279	746
Capri		12.26	8.99	1.68	949.74	1.33	178.38	20890	<MDL	1626
	%ERROR	2.28	10.58	4.44	8.56	32.58	4.01	22	33	45

After 159 Days

Qm

		Cu	Ni	Cd	Al	Cr	Zn	Pb(ppb)	As(ppb)
Decew		10.79	7.47	1.55	857.37	1.49	80.08	5372	1546
Glend		10.95	8.09	1.49	1396.24	3.35	91.01	8566	3929
Nia Coll		9.70	7.41	1.00	1435.32	3.28	81.17	2394	2763
Site 10		12.95	7.51	0.70	1043.40	3.57	81.98	2722	2399
Site 16		12.37	8.48	0.69	1043.78	4.02	81.78	1555	5015
Gibs		14.47	5.77	1.19	711.04	6.26	86.14	438	3343
Capri		N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	%ERROR	5.14	3.84	4.62	6.57	10.28	2.69	9.15	12.04

Unitless Ratio's Comparing Initial Pt Colbourne to Active Biomonitors

69 Days ZM	Cu	Ni	Cd	Al	Cr	Zn	Pb	As	Se
Decew	0.84	1.05	1.28	19.93	1.06	0.84	3.07	0.20	1.06
Glendale	0.78	1.27	0.99	17.74	1.80	0.82	3.26	0.04	0.37
N.C.	0.74	1.07	1.01	8.78	0.91	0.81	2.98	0.00	0.35
Site 10	0.73	0.62	0.76	13.90	4.75	0.66	2.86	0.00	0.55
Site 16	0.69	1.29	0.71	9.11	3.28	0.80	3.47	0.44	0.46
Lake Gibs	1.53	0.81	0.96	6.68	2.21	0.91	2.07	0.38	0.10
Capri	0.97	1.19	1.12	13.93	1.42	1.40	9.75	0.00	0.35

69 Days QM	Cu	Ni	Cd	Al	Cr	Zn	Pb	As	Se
Decew	0.73	1.65	1.65	17.10	1.21	0.47	1.71	1.33	1.86
Glendale	0.72	1.45	1.47	22.60	1.51	0.51	1.88	0.42	0.69
N.C.	0.73	1.71	0.97	17.28	0.70	0.45	2.14	0.75	1.40
Site 10	0.70	2.57	1.21	12.65	29.90	0.55	1.30	0.63	0.00
Site 16	0.66	1.51	0.84	22.84	1.92	0.41	2.56	1.03	0.00
Lake Gibs	0.82	1.17	1.30	13.96	6.89	0.65	2.12	0.72	0.48
Capri	0.91	1.56	2.04	18.82	1.36	1.33	9.74	0.00	1.05

159 Days QM	Cu	Ni	Cd	Al	Cr	Zn	Pb	As
Decew	0.80	1.29	1.87	16.99	1.52	0.60	2.51	0.87
Glend	0.81	1.40	1.80	27.67	3.42	0.68	3.99	2.21
Nia Coll	0.72	1.28	1.20	28.44	3.35	0.61	1.12	1.56
Site 10	0.96	1.30	0.84	20.67	3.65	0.61	1.27	1.35
Site 16	0.92	1.47	0.83	20.68	4.11	0.61	0.73	2.82
Lake Gibs	1.08	1.00	1.44	14.09	6.40	0.64	0.20	1.88
Capri	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

Active 'Big Clam' Biomonitors Values after 159 days All values are ppm unless otherwise stated.

	Cu	Ni	Cd	Al	Cr	Zn	Pb(ppb)	As(ppb)	Length mm
SHPP Ell 11 Gut	7.39	2.03	0.80	5.03	1.28	189.23	<MDL	1239.74	92
SHPP Ell 11 Muscle	3.75	1.87	0.51	12.31	0.59	60.55	<MDL	1327.89	92
SHPP Ell 11 H/R + gonads	26.96	4.90	1.45	62.55	0.35	392.97	1165.50	1113.05	92
SHPP Ell 11 Foot	5.31	0.28	0.11	51.47	1.66	86.33	1973.19	573.26	92
SHPP Ell 11 Kid + gill & gut	24.36	0.90	20.27	4.11	1.23	232.25	<MDL	<MDL	92
SHPP Ell 11 Mantle	7.22	2.72	1.11	27.65	1.73	267.12	1045.52	3803.21	92
SHPP Ell 11 Gill	18.05	3.75	1.37	17.49	0.91	354.35	<MDL	5823.01	92
SHPP Ell 11 Gill + Gonads	29.46	12.57	0.06	33.88	1.72	355.91	<MDL	3185.12	92
SHPP Ell 31 Kid + gill	22.20	2.54	99.90	23.11	1.86	190.59	6894.53	<MDL	91
SHPP Ell 31 Foot	5.75	<MDL	0.47	1.09	1.21	81.03	2737.04	371.40	91
SHPP Ell 31 H/R + gonads	39.76	5.96	1.42	8.41	<MDL	378.82	<MDL	<MDL	91
SHPP Ell 31 Gill	22.00	6.49	3.65	15.69	2.88	381.45	<MDL	6528.76	91
SHPP Ell 31 Mantle	10.36	3.19	5.04	74.96	2.95	237.41	1969.75	3112.68	91
SHPP Ell 31 Gut	6.93	1.00	1.59	7.19	1.26	129.86	<MDL	2723.58	91
SHPP Ell 31 Muscle	4.47	1.03	1.09	9.76	0.71	71.43	966.22	1644.93	91
SHPP Ana 27/31 Gill	22.00	6.49	3.65	15.69	2.88	381.45	<MDL	6528.76	101
SHPP Ana 27/31 Foot	9.02	0.24	0.59	5.40	0.82	108.79	2602.32	1018.63	101
SHPP Ana 27/31 Gut	10.66	1.91	1.63	55.60	0.56	108.19	<MDL	1191.78	101
SHPP Ana 27/31 Muscle	6.24	1.22	1.40	19.84	0.42	69.54	2331.12	3221.21	101
SHPP Ana 27/31 Kid	29.96	0.80	96.86	42.11	1.20	187.72	3138.30	<MDL	101
SHPP Ana 27/31 H/R	30.84	2.14	6.01	<MDL	<MDL	151.54	18861.21	1699.29	101
Decew Ana 8 Foot	4.65	1.31	1.54	7.70	<MDL	101.59	1520.23	1077.85	104.5
Decew Ana 8 Gill	14.55	7.31	7.58	7.86	5.19	323.63	1622.14	7229.42	104.5
Decew Ana 8 Gut	8.52	1.56	4.68	4.41	0.06	129.70	7757.42	1637.57	104.5
Decew Ana 8 H/R	21.20	3.08	10.11	5.14	<MDL	117.88	25322.13	66939.78	104.5
Decew Ana 8 Kid	30.99	11.04	125.62	12.82	<MDL	160.81	86755.85	24306.02	104.5
Decew Ana 8 Mant	7.68	3.80	8.86	968.99	3.06	182.46	13339.16	3208.67	104.5
Decew Ana 8 Muscle	5.93	2.03	2.60	111.07	0.95	66.76	<MDL	3837.48	104.5
Glend Ana 12 Foot	4.91	<MDL	0.83	6.19	0.83	96.77	<MDL	4445.81	104.5
Glend Ana 12 Gill	11.25	5.53	5.37	15.02	4.84	439.71	<MDL	9717.66	104.5
Glend Ana 12 Gut	8.75	0.85	4.75	11.64	1.27	127.49	3721.86	2636.28	104.5
Glend Ana 12 H/R	42.91	<MDL	2.60	15.65	0.83	127.53	40380.11	25900.55	104.5
Glend Ana 12 Kid + gill	19.85	2.73	114.95	33.19	7.86	172.08	19146.33	3622.64	104.5
Glend Ana 12 Mant	8.15	1.77	8.84	88.12	1.38	190.81	2765.85	1559.76	104.5
Glend Ana 12 Muscle	3.69	<MDL	1.47	8.01	0.90	60.03	571.30	325.87	104.5
Nia Coll Ana 4 Foot	7.84	<MDL	1.00	18.74	0.88	114.09	642.50	<MDL	106
Nia Coll Ana 4 Gill	10.52	4.22	5.90	17.93	4.76	469.54	<MDL	7576.86	106
Nia Coll Ana 4 Gut	7.75	0.63	4.63	13.58	1.38	150.25	4310.13	1109.77	106
Nia Coll Ana 4 H/R	37.97	<MDL	4.95	55.84	5.41	191.15	26375.26	<MDL	106
Nia Coll Ana 4 Kid	18.22	1.72	96.86	60.06	2.16	238.07	9180.69	5241.38	106
Nia Coll Ana 4 Mant	7.89	1.43	6.61	65.49	1.08	234.76	7960.84	1852.04	106
Nia Coll Ana 4 Muscle	4.78	<MDL	1.26	18.82	0.75	85.35	2387.20	965.58	106
Nia Coll Ell 36 Foot	4.58	0.73	1.21	7.88	0.81	96.86	2642.70	370.13	92
Nia Coll Ell 36 Gill + Gonads	18.52	10.68	1.17	23.84	0.20	292.48	6788.37	1379.12	92
Nia Coll Ell 36 Gut	6.09	3.59	3.51	17.63	2.27	336.05	1084.67	7480.27	92
Nia Coll Ell 36 H/R	27.28	11.78	3.06	142.78	<MDL	358.55	15301.91	7337.58	92
Nia Coll Ell 36 Kid	18.66	14.54	72.53	7.85	9.35	262.56	8555.59	1528.94	92
Nia Coll Ell 36 Mant	6.46	5.33	2.52	30.77	4.85	404.34	<MDL	7800.31	92
Nia Coll Ell 36 Muscle	5.73	1.79	1.65	24.81	2.26	131.55	979.61	683.71	92
Nia Coll Ell 36 Gill	9.02	4.31	4.31	19.35	4.04	372.64	605.91	4889.40	92

	Cu	Ni	Cd	Al	Cr	Zn	Pb(ppb)	As(ppb)	Length mm
Capri Ana 26 Foot	10.93	0.69	5.50	17.11	3.58	103.18	3041.24	1794.65	118
Capri Ana 26 Gill	29.14	7.16	19.45	21.18	5.29	555.70	<MDL	46262.42	118
Capri Ana 26 Gut	11.99	1.32	10.58	7.86	3.43	113.73	7686.12	3708.72	118
Capri Ana 26 H/R	55.99	<MDL	7.81	122.66	22.75	25.75	3217.98	6696.63	118
Capri Ana 26 Kid + gill	25.96	5.53	136.95	32.44	6.67	310.85	6479.05	8624.51	118
Capri Ana 26 Mant	15.51	2.40	19.53	109.57	2.94	189.15	3004.03	5799.47	118
Capri Ana 26 Muscle	5.94	<MDL	3.63	30.07	1.34	71.78	248.89	1590.96	118
Capri Ana 1 Foot	7.30	1.19	1.19	37.91	3.43	108.10	492.80	481.00	109
Capri Ana 1 Gill	16.64	5.25	9.08	29.79	5.55	384.15	171.76	9270.11	109
Capri Ana 1 Gut	10.45	0.16	4.05	29.24	1.90	130.97	2829.38	1698.33	109
Capri Ana 1 H/R	29.45	0.94	4.94	260.48	6.13	86.74	6027.67	25157.23	109
Capri Ana 1 Kid + gill	36.89	1.64	150.33	251.60	6.16	118.04	9569.32	2323.29	109
Capri Ana 1 Mant	18.01	<MDL	11.81	82.41	2.23	184.26	5744.48	2315.39	109
Capri Ana 1 Muscle	9.14	0.82	2.38	12.60	1.90	80.75	201.39	<MDL	109
Site 10 Ana 27 Foot	8.44	2.67	3.96	29.84	3.22	118.22	5471.88	2406.25	110
Site 10 Ana 27 Gill	30.81	7.97	18.39	30.64	3.91	423.23	1251.71	29132.27	110
Site 10 Ana 27 Gut	10.93	2.04	8.60	21.46	2.10	141.03	3379.89	5948.79	110
Site 10 Ana 27 H/R	40.77	6.61	11.57	193.53	0.62	70.59	24482.64	17123.97	110
Site 10 Ana 27 Kid + gill & gut	28.89	6.40	133.34	106.06	5.57	446.33	5240.46	13982.07	110
Site 10 Ana 27 Mant	13.30	3.13	16.33	143.69	2.96	272.26	3524.01	6035.25	110
Site 10 Ana 27 Muscle	7.51	1.61	6.94	64.24	0.83	87.07	1197.47	2338.89	110
Site 16 Ana 2 Foot	8.15	0.77	1.14	9.67	2.08	115.29	1567.15	234.09	114
Site 16 Ana 2 Gill	14.25	8.16	4.01	26.02	8.88	362.28	<MDL	6552.66	114
Site 16 Ana 2 Gut	8.34	1.49	2.12	32.90	1.92	102.52	2790.44	1265.38	114
Site 16 Ana 2 H/R	23.19	<MDL	5.88	225.86	4.55	114.34	2902.33	2317.12	114
Site 16 Ana 2 Kid	28.89	12.18	134.87	323.75	8.62	153.07	13252.41	4266.67	114
Site 16 Ana 2 Mant	9.07	1.28	6.34	98.54	2.79	159.93	3753.14	1125.74	114
Site 16 Ana 2 Muscle	5.41	1.83	1.34	45.55	2.11	54.98	1473.20	385.79	114
Site 16 Ell 25 Foot	8.99	0.25	9.07	6.32	1.43	123.36	1757.70	1129.57	117
Site 16 Ell 25 Gill	10.50	4.65	7.00	20.44	4.30	376.31	1014.89	7003.61	117
Site 16 Ell 25 Gut	6.23	2.12	3.34	17.18	3.25	174.12	1192.33	6080.25	117
Site 16 Ell 25 H/R	21.26	4.16	4.30	93.30	7.02	329.43	2892.20	6918.54	117
Site 16 Ell 25 Kid + gill	16.49	12.84	103.16	26.14	7.95	261.67	21226.11	7806.32	117
Site 16 Ell 25 Mant	7.83	3.16	6.64	31.26	4.08	256.55	928.54	5228.46	117
Site 16 Ell 25 Muscle	4.51	0.37	1.84	12.16	1.26	76.40	1307.17	1524.65	117
Gibs Ana 22 Foot	6.28	1.03	1.98	<MDL	2.97	121.30	430.91	1089.77	132
Gibs Ana 22 Gill	15.07	7.25	8.42	18.54	4.77	451.12	<MDL	12493.38	132
Gibs Ana 22 Gut	8.96	0.55	8.01	18.71	2.84	107.44	3647.43	2157.49	132
Gibs Ana 22 H/R	26.60	<MDL	9.29	<MDL	9.16	73.24	1654.66	6782.61	132
Gibs Ana 22 Kid	27.56	11.19	172.11	<MDL	18.68	204.12	23301.08	3263.54	132
Gibs Ana 22 Mant	9.92	5.42	17.15	186.13	8.21	174.28	1861.43	6114.69	132
Gibs Ana 22 Muscle	5.45	2.08	2.20	23.66	4.60	92.83	649.49	284.75	132